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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/AU98/00412 <b>(22) International Filing Date:</b> 2 June 1998 (02.06.98) <b>(30) Priority Data:</b> PO 7104 2 June 1997 (02.06.97) AU <b>(71) Applicants (for all designated States except US):</b> ISHIKAWA-JIMA-HARIMA HEAVY INDUSTRIES COMPANY LIMITED [JP/JP]; 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo 100 (JP). BHP STEEL (JLA) PTY. LTD. [AU/AU]; 600 Bourke Street, Melbourne, VIC 3000 (AU). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> STREZOV, Lazar [AU/AU]; 7 Marin Street, Adamstown, NSW 2289 (AU). <b>(74) Agent:</b> GRIFFITH, Hack; 509 St. Kilda Road, Melbourne, VIC 3004 (AU).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> AMORPHOUS OR GLASSY ALLOY SURFACED ROLLS FOR THE CONTINUOUS CASTING OF METAL STRIP  <div data-bbox="451 1144 1172 1423" data-label="Image"> </div> <p style="text-align: right;">(x50)</p> <b>(57) Abstract</b>  <p>Twin roll casting has been applied with some success to non-ferrous metals, which solidify rapidly on cooling. The same, however, is not true for ferrous metals, as it has not been possible to achieve sufficiently rapid and even cooling of metal over the casting surfaces of the rolls. This problem has been overcome by utilising a metallic surface for the rolls, which has a high affinity for the molten steel of the casting pool and a melting temperature greater than the temperature of the casting surface. The molten steel produces extremely good wetting of the casting surface of the roll, resulting in a wetting angle of the molten steel on the casting surface of less than 40°. Preferably, this wetting angle is less than 20° and the casting surface has an Arithmetic Mean Roughness Value (Ra) of less than 10 microns. These desirable properties on the roll surface are achieved by selecting an at least partially amorphous alloy of two constituents. Preferably, the alloy is a fully amorphous alloy of the nickel-phosphorus system containing about 10 % phosphorus and the balance nickel, which may be applied by electroless coating. This roll surface prevents the build-up of iron oxide on the casting surfaces of the rolls, which build-up interferes with the uniform conduction of heat away from the molten steel, resulting in simultaneous solidification of the <math>\delta</math> and <math>\gamma</math> iron phases (0.01-0.18 %C), which causes a surface defect, known as "crocodile-skin". The net effect of utilising this amorphous alloy for the surface of the casting roll is a superior and uniform conduction of heat away from the molten steel, rapid transformation of the steel's microstructure into the wholly austenitic (<math>\gamma</math>) region, exhibited by fine prior austenite grain boundaries conforming to dendritic grain boundaries and absence of "crocodile-skin" surface defects on the cast strip.</p>		

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## AMORPHOUS OR GLASSY ALLOY SURFACED ROLLS FOR THE CONTINUOUS CASTING OF METAL STRIP

TECHNICAL FIELD

This invention relates to the casting of metal strip. It has particular but not exclusive application to  
5 the casting of ferrous metal strip.

It is known to cast metal strip by continuous casting in a twin roll caster. In this technique molten metal is introduced between a pair of contra-rotated horizontal casting rolls which are cooled so that metal  
10 shells solidify on the moving roll surfaces and are brought together at the nip between them to produce a solidified strip product delivered downwardly from the nip between the rolls. The term "nip" is used herein to refer to the general region at which the rolls are closest together.  
15 The molten metal may be poured from a ladle into a smaller vessel or series of vessels from which it flows through a metal delivery nozzle located above the nip so as to direct it into the nip between the rolls, so forming a casting pool of molten metal supported on the casting surfaces of  
20 the rolls immediately above the nip and extending along the length of the nip. This casting pool is usually confined between side plates or dams held in sliding engagement with end surfaces of the rolls so as to dam the two ends of the casting pool against outflow, although alternative means  
25 such as electromagnetic barriers have also been proposed.

Although twin roll casting has been applied with some success to non-ferrous metals which solidify rapidly on cooling, there have been problems in applying the technique to the casting of ferrous metals. One particular  
30 problem has been the achievement of sufficiently rapid and even cooling of metal over the casting surfaces of the rolls.

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Our United States Patent 5,520,243 (International Patent Application PCT/AU93/00593) describes a development by which the cooling of metal at the casting surface of the rolls can be dramatically improved by taking steps to

5 ensure that the roll surfaces have certain smoothness characteristics in conjunction with the application of relative vibratory movement between the molten metal of the casting pool and the casting surfaces of the rolls. Specifically that Patent discloses that the application of

10 vibratory movements of selected frequency and amplitude make it possible to achieve a totally new effect in the metal solidification process which dramatically improves the heat transfer from the solidifying molten metal, the improvement being such that the thickness of the metal

15 being cast at a particular casting speed can be very significantly increased or alternatively the speed of casting can be substantially increased for a particular strip thickness. The improved heat transfer is associated with a very significant refinement of the surface structure

20 of the cast metal.

Our United States Patent 5,584,338 describes a further development whereby effective relative vibration between the molten metal of the casting pool and the casting surface can be induced by the application of sound

25 waves to the molten metal of the casting pool whereby increased heat transfer and solidification structure refinement can be achieved by the application of sound waves in the sonic range at quite low power levels.

Our further United States Patent 5,720,336

30 describes the results of research on the heat transfer mechanism occurring at the interface between the casting surface and the molten metal of the casting pool and

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discloses that the heat flux on solidification can be controlled and enhanced by ensuring that the casting surfaces are each covered by a layer of a material which is at least partially liquid at the solidification temperature of the metal, whereby it is possible to achieve improved heat transfer without necessarily generating relative vibration between the casting pool and the rolls.

In the ensuing description it will be necessary to refer to a quantitative measure of the smoothness of casting surfaces. One specific measure used in our experimental work and helpful in defining the scope of the present invention is the standard measure known as the Arithmetic Mean Roughness Value which is generally indicated by the symbol  $R_a$ . This value is defined as the arithmetical average value of all absolute distances of the roughness profile from the centre line of the profile within the measuring length  $l_m$ . The centre line of the profile is the line about which roughness is measured and is a line parallel to the general direction of the profile within the limits of the roughness-width cut-off such that sums of the areas contained between it and those parts of the profile which lie on either side of it are equal. The Arithmetic Mean Roughness Value may be defined as

$$R_a = \frac{1}{l_m} \int_{x=0}^{x=l_m} |y| dx$$

Although the above described developments have enabled the achievement of high solidification rates with the casting of ferrous metal strip it has proved very

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difficult to produce strip which does not exhibit the surface defect known as "crocodile-skin". This defect occurs when  $\delta$  and  $\gamma$  iron phases solidify simultaneously in shells on the casting surfaces of the rolls in a twin roll  
5 caster under circumstances in which there are variations in heat flux through the solidifying shells. The  $\delta$  and  $\gamma$  iron phases have differing hot strength characteristics and the heat flux variations then produce localised distortions in the solidifying shells which come together at the nip  
10 between the casting rolls and result in the crocodile-skin defects in the surfaces of the resulting strip. Previously this problem has been addressed by endeavouring to keep the build up of oxides on the casting rolls within strict limits by complicated roll cleaning devices.

15 A light oxide deposit can be beneficial in ensuring a controlled even flux during metal solidification on to the casting roll surfaces. The oxide deposit melts as the roll surfaces enter the molten metal casting pool and assists in establishing a thin liquid interface layer  
20 between the casting surface and the molten metal of the casting pool to promote good heat flux. However, if there is too much oxide build up the melting of the oxides produces a very high initial heat flux but the oxides then resolidify with the result the heat flux decreases rapidly.  
25 The resulting heat flux variations in the solidifying shells produce the localised distortions leading to crocodile-skin surface defects.

We have now determined that the deleterious effect of the metal oxidation products can be avoided and very  
30 high solidification rates can be achieved if the casting surfaces of the rolls are formed of a material which has a high affinity for the molten metal of the casting pools so

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as to produce extremely good wetting of the casting surface by the molten metal. If there is sufficiently good wetting by the molten metal it is possible for solidification to proceed so rapidly that there is insufficient time for any significant quantities of oxidation products to form. In the case of steel melts it is also possible to achieve rapid solidification of the steel melt into a single phase solid structure thereby effectively avoiding any potential for crocodile-skin defects.

10 DISCLOSURES OF THE INVENTION

According to the invention there is provided a method for continuously casting metal strip of the kind in which a casting pool of molten metal is formed in contact with a moving casting surface such that metal solidifies from the pool onto the moving casting surface, wherein the casting surface is provided by a solid coating on a heat conductive body and the coating is formed of a material such that the wetting angle of said molten metal on the casting surface is less than  $40^\circ$  and which has a melting temperature greater than the temperature of the casting surface during metal solidification.

Preferably further the coating is formed of a material such that the wetting angle of the molten metal on the casting surface is less than  $20^\circ$ .

25 Preferably the coating surface has an Arithmetic Mean Roughness Value ( $R_a$ ) of less than 10 microns.

The coating material should be chosen so as not to melt or to dissolve in said molten metal at the temperature of the casting surface during solidification.

30 Preferably, the coating material is at least partially amorphous. It may, for example, comprise an amorphous alloy of two metals. One of those metals may be



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phosphorous.

More specifically, the coating material may comprise an amorphous nickel-phosphorous alloy containing about 10% phosphorous.

5           The heat conductive body may be a body of copper or a copper alloy.

The molten metal may be a ferrous metal.

More specifically, the molten metal may be molten steel. In this case, the choice of a coating material on  
10 which the molten steel has a low wetting angle enables solidification of the steel into a single phase solid structure on the casting surface.

Accordingly the invention also provides a method for continuously casting steel strip of the kind in which a  
15 casting pool of molten steel is formed in contact with a moving casting surface such that steel solidifies from the casting pool onto the moving casting surfaces, wherein the casting surface is provided by a solid coating on a heat conductive body and the coating is formed of a material  
20 such that the wetting angle of the molten steel on the casting surface is less than 40° and which has a melting temperature greater than the temperature of the casting surface during metal solidification, and wherein the steel solidifies into a single phase solid structure on the  
25 casting surface which phase does not transform before the strip has left the casting surface.

The method of the present invention may be carried out in a twin roll caster.

Accordingly the invention further provides a method  
30 of continuously casting metal strip of the kind in which molten metal is introduced into the nip between a pair of parallel casting rolls via a metal delivery nozzle disposed

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above the nip to create a casting pool of molten metal supported on casting surfaces of the rolls immediately above the nip and the casting rolls are rotated to deliver a solidified metal strip downwardly from the nip, wherein  
5 the casting surfaces of the rolls are provided by solid coatings on heat conductive roll bodies which coatings are formed of a material such that the wetting angle of said molten metal on the casting surfaces of the rolls is less than 40° and which material has a melting temperature  
10 greater than the temperature of the casting surfaces during metal solidification.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In order that the invention may be more fully explained the results of experimental work carried out to  
15 date will be described with reference to the accompanying drawings in which:

Figure 1 illustrates experimental apparatus for determining metal solidification rates under conditions simulating those of a twin roll caster;

20 Figure 2 illustrates an immersion paddle incorporated in the experimental apparatus of Figure 1;

Figure 3 illustrates thermal resistance values obtained during solidification of a typical steel sample in the experimental apparatus;

25 Figure 4 illustrates the relationship between wettability of an interface layer and measured heat flux and interface resistance;

Figures 5 illustrates the effect of wettability on the resistance to nucleation;

30 Figure 6 illustrates shell surface temperatures occurring in steel shells deposited on chromium substrates;

Figure 7 plots the results of heat flux

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measurements on steel shells deposited on nickel-phosphorous substrate and on chromium substrates;

Figure 8 plots K-value measurements on steel shells deposited during dip tests using nickel-phosphorous alloy  
5 and chromium substrates;

Figures 9 and 10 are photomicrographs of steel shells deposited in the dip tests to which Figure 8 refers;

Figure 11, plots K-value measurements on steel shells deposited during further dip tests using various  
10 substrates and steel melt compositions;

Figure 12 to 16 are photomicrographs of steel shells deposited during the dip test to which Figure 11 refers;

Figure 17 is a plan view of a continuous strip  
15 caster which is operable in accordance with the invention;

Figure 18 is a side elevation of the strip caster shown in Figure 17;

Figure 19 is a vertical cross-section on the line 19-19 in Figure 17;

20 Figure 20 is a vertical cross-section on the line 20-20 in Figure 17; and

Figure 21 is a vertical cross-section on the line 21-21 in Figure 17.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

25 Figures 1 and 2 illustrate a metal solidification test rig in which a 40 mm x 40 mm chilled block is advanced into a bath of molten steel at such a speed as to closely simulate the conditions at the casting surfaces of a twin roll caster. Steel solidifies onto the chilled block as it  
30 moves through the molten bath to produce a layer of solidified steel on the surface of the block. The thickness of this layer can be measured at points

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throughout its area to map variations in the solidification rate and therefore the effective rate of heat transfer at the various locations. It is thus possible to produce an overall solidification rate as well as total heat flux measurements. It is also possible to examine the microstructure of the strip surface to correlate changes in the solidification microstructure with the changes in observed solidification rates and heat transfer values.

The experimental rig illustrated in Figures 1 and 2 comprises an induction furnace 1 containing a melt of molten metal 2 in an inert atmosphere which may for example be provided by argon or nitrogen gas. An immersion paddle denoted generally as 3 is mounted on a slider 4 which can be advanced into the melt 2 at a chosen speed and subsequently retracted by the operation of computer controlled motors 5.

Immersion paddle 3 comprises a steel body 6 which contains a substrate 7 in the form of a chrome plated copper disc of 46 mm diameter and 18 mm thickness. It is instrumented with thermo-couples to monitor the temperature rise in the substrate which provides a measure of the heat flux.

Tests carried out on the experimental rig illustrated in Figures 1 and 2 have demonstrated that the observed solidification rates and heat flux values as well as the microstructure of the solidified shell are greatly affected by the conditions at the shell/substrate interface during solidification. The tests have shown that high heat flux and solidification rates can be achieved with smooth substrate surfaces and this can generate refined grain structure of the solidified metal.

During solidification the total resistance to heat

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flow from the melt to the substrate (heat sink) is governed by the thermal resistances of the solidifying shell and the shell/substrate interface. Under the conditions of conventional continuously cast sections (slabs, blooms or  
5 billets), where solidification is completed in around 30 minutes, the heat transfer resistance is dominated by the solidifying shell resistance. However, our experimental work has demonstrated that under thin strip casting conditions, where solidification is completed in less than  
10 a second, the heat transfer resistance is dominated by the interface thermal resistance at the surface of the substrate.

The heat transfer resistance is defined as

15 
$$R_{(t)} = \Delta T_{(t)} / \Delta Q_{(t)}$$

where  $Q$ ,  $\Delta T$  and  $t$  are heat flux, temperature difference between melt and substrate and time, respectively.

Figure 3 illustrates thermal resistance values  
20 obtained during solidification of a typical manganese killed low carbon steel sample in the test rig. This shows that the shell thermal resistance contributes only a small proportion of the total thermal resistance which is dominated by the interface thermal resistance. The  
25 interface resistance is initially determined by the melt/substrate interface resistance and later by the shell/substrate interface thermal resistance. Furthermore, it can be seen that the interface thermal resistance does not significantly change in time which indicates that it  
30 will be governed by the melt/substrate thermal resistance at the initial melt/substrate contact.

For a two-component system (melt and substrate),

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the melt/substrate interface resistance and heat flux are determined by the wettability of the melt on a particular substrate. This is illustrated in Figure 4 which shows how interface resistance increases and heat flux decreases with increasing wetting angle which corresponds with reducing wettability.

The importance of wetting of the substrate by the melt was demonstrated by the developmental work described in our aforesaid United States Patent 5,520,243 (International Patent Application PCT/AU93/00593) which discloses application of vibratory movements. The application of vibratory movements was for the purpose of promoting wetting of the substrate and increasing the nucleation density for the melt solidification. The mathematical model described at page 10 of that case proceeded on the basis that full wetting was required and considered the vibrational energy required to achieve this. In the experimental work which verified this analysis it was shown that significant improvement in heat flux could not be obtained unless the substrate was smooth. More specifically, it is necessary for the substrate to have an Arithmetic Mean Roughness Value ( $R_a$ ) of less than 5 microns in order to obtain full wetting of the substrate, even with the application of vibration energy. These results are appropriate for substrates of chromium on which steel melts have moderately good wettability. However, by the present invention the casting surfaces of the rolls can be formed of a material which has a much higher affinity for steel melts so producing much better wetting than can be achieved with a chrome surface. In these circumstances the smoothness of the substrate is not particularly critical although it is desirable in practice that the casting

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surfaces have an Arithmetic Mean Roughness Value ( $R_a$ ) of less than 10 microns in order to produce strip having a reasonably good surface finish and a refined microstructure.

5           For metal solidification onto a smooth substrate it can be assumed that solidification will proceed at heterogeneous nucleation sites throughout the substrate. The effect of wetting angle on dimensionless free energy of nucleation according to such classical heterogeneous  
10 nucleation theory is illustrated in Figure 5 which shows the manner in which the dimensionless free energy barrier factor increases with increasing wetting angle ie with reducing wetting effectiveness. Wetting angles of  $40^\circ$  and less represent very good wetting effectiveness at which  
15 there is a negligible energy barrier to solidification. Wetting angles above  $75^\circ$  represent poor wetting above which there will be a significant energy barrier to metal solidification.

          Twin roll strip casters for casting ferrous metals  
20 have traditionally employed casting rolls with chromium or nickel casting surfaces generally produced by plating. Such surfaces are tough and are generally able to withstand the thermal stresses associated with strip casting. Moreover, steel melts have moderately good wettability on  
25 chromium and nickel surfaces enabling effective heat flux values to be achieved. We have also determined that the metal oxides deposited from typical steel melts used for strip casting have a high affinity for chromium and nickel and they therefore exhibit good wettability on such casting  
30 surfaces ie very low wetting angles. This means that there is a very strong tendency for an oxide coating to spread over the casting surfaces and to build up as casting

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proceeds.

Figure 6 illustrates the measurement of shell surface temperatures occurring in steel shells deposited on chromium surfaces in the dip tested illustrated in Figures 1 and 2 for both a clean substrate surface and a surface with a heavy oxide deposit. It will be seen that for smooth substrate surface the surface of the solidifying shell decreases smoothly in temperature as solidification progresses. Where the substrate has a heavy oxide covering the shell initially proceeds with under-cooling down to a temperature approaching 1200°C at which stage there is a sudden reversal and the temperature of the shell increases. It is thought that the under-cooling proceeds while the oxides are in liquid form but as the temperature approaches 1200°C the oxides solidify to provide nucleation sites for metal solidification. However, the solid oxides then provide a barrier to heat flux with consequent loss of cooling effectiveness and the surface temperature of the shell increases. Previously it was thought that this effect could only be overcome by careful cleaning of the rolls during casting to maintain the oxide levels within a very strict range. However, we have now determined that by forming the casting surfaces from an alternative material which causes extremely good wetting by the steel melt it is possible to cause the steel melt to solidify without significant under-cooling below the liquidus temperature. Such cooling may proceed so rapidly that there is no time for oxidation products to form on the casting surfaces so that solidification proceeds without any significant interference by deposited oxidation products. Specifically these results have been demonstrated by dip testing in the apparatus as illustrated in Figures 1 and 2 using cooling



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substrates of a nickel-phosphorous alloy comprising 10% phosphorous. This alloy can be coated onto a cooling roll by an electroless process and it promotes very good wetting by steel melts. For most steel melts the wetting angle on  
5 this coating would be of the order of 25° or less.

Figure 7 plots heat flux measurements obtained on solidification of a carbon steel onto substrates of the nickel-phosphorous alloy compared with heat flux measurements on solidification of shells of the same steel  
10 onto chrome substrates. The carbon steel in these tests had the following composition which we designate an MO6 steel:

Carbon	0.06% by weight
Manganese	0.6% by weight
15 Silicon	0.28% by weight
Aluminium	≤ 0.002% by weight
Melt free oxygen	60-100 parts per million.

Figure 8 provides the results of measurements of K-value (an indication of heat flux) for multiple dip tests  
20 using a carbon steel melt of the above composition and with the nickel-phosphorous alloy and chromium substrates. It will be seen that the results in both Figures 7 and 8 demonstrate that the nickel-phosphorous alloy substrates resulted in much higher heat flux than the normal chrome  
25 substrates. In the case of the nickel-phosphorous alloy substrate there was a variation in heat flux over different tests and particularly a decreasing K-value throughout successive dip tests in the results shown in Figure 8. These variations were due to melting of the nickel-  
30 phosphorous alloy substrate surface as testing proceeded. Accordingly in order to achieve a long-life coating in a commercial strip caster for casting steel strip at high

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melt temperatures it would be desirable to modify this particular alloy composition in order to increase its melting temperature. However, the tests demonstrate the dramatically improved results which can be achieved with  
5 low wetting angles and the nickel-phosphorous alloy as tested would be entirely suitable for use in casting of other metals such as copper.

Figures 9 and 10 are photomicrographs of M06 steel shells deposited onto substrates of nickel-phosphorous  
10 alloy in the case of Figure 9 and a traditionally chromium substrate in the case of Figure 10, both photomicrographs being shown to a magnification of x100. It will be seen that the shell deposited onto the nickel-phosphorous alloy substrate is almost twice as thick as the shell deposited  
15 on the chromium substrate, reflecting the much higher heat flux and more rapid solidification obtained with the nickel-phosphorous alloy substrate. This demonstrates that very much higher solidification rates are achievable and that accordingly the invention will permit strip casting to  
20 proceed at dramatically higher production rates than have hitherto been thought possible. Moreover, it will be seen that the microstructure of the shell deposited on the nickel-phosphorous alloy substrate is significantly finer than that deposited on the traditional chrome substrate and  
25 is moreover remarkably even throughout the shell. This microstructure exhibits prior austenite grain boundaries that exactly follow dendritic grain boundaries demonstrating that the liquid carbon steel has solidified directly into austenite. With this solidification process  
30 there is no potential for the development of crocodile-skin defects since these defects arise only when both  $\delta$  and  $\gamma$  phases are present in the solidifying steel shells.

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It has been found that the enhanced wettability of the nickel-phosphorous alloy is due to its amorphous structure. Liquids will in general have a high surface affinity for other liquids since they have no preferential orientation and we have now found that a similar effect can be produced when wetting an amorphous solid. Wettability of a liquid metal on a coating surface can accordingly be dramatically increased if the coating material is totally amorphous. The nickel-phosphorous alloy with a 10% phosphorous content, as used in the tests to which Figures 8 and 9 refer, is a substantially eutectic composition and can readily be deposited by an electroless process so as to have an effectively totally amorphous structure. If the phosphorous content is varied so as to depart significantly from the eutectic composition the deposited two-metal alloy coating will exhibit a partially crystalline structure rather than being totally amorphous. Moreover, a crystalline structure can also be produced by annealing the coating at elevated temperature after deposition, a phenomenon that is used to increase hardness in some coating applications.

In order to demonstrate the effect of an amorphous coating in enhancing wettability and heat flux in accordance with the invention, we have conducted a series of further tests in which steel melts have been solidified on nickel-phosphorous alloy substrates of varying phosphorous composition, on nickel-phosphorous alloy substrates which were annealed at elevated temperature prior to testing and also on smooth nickel substrates to provide standard or control data. Moreover, in order to further demonstrate the direct solidification of steel directly into austenite dendrites in accordance with the

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invention the further tests included the deposition of shells from a peritectic grade steel which would normally produce gross distortions on solidification through solidification into  $\delta$  and  $\gamma$  phases simultaneously. The results of this further testing are illustrated by Figures 11 to 16.

Figure 11 provides the results of measurements of K-value for multiple dip tests. Dip tests 1-27 all used steel melts having the above described MO6 composition. In tests 1-9 steel shells were deposited on both a smooth nickel substrate having an  $R_a$  value of 5.6 and on a nickel-phosphorous alloy substrate having a 10% phosphorous content and a Mean Roughness Value ( $R_a$ ) of 8.7.

The nickel-phosphorous substrate used in tests 1-9 was deposited by an electroless process and was not annealed. It will be seen that very high K-values were achieved with this substrate as compared with the smooth nickel substrate used as a control. These results are quite similar to those shown in Figure 8.

Figure 8 further shows results of tests 10-15 in which the nickel substrate was maintained as a control comparison against results for solidification onto a nickel-phosphorous alloy substrate having a phosphorous content of 5% and an Arithmetic Mean Roughness Value ( $R_a$ ) of 6.6. It will be seen that the K-value achieved with the 5% phosphorous alloy was significantly less than that with the 10% phosphorous alloy of tests 1-9, even though a smoother substrate was employed, demonstrating that the partially crystalline structure inevitable in the 5% phosphorous alloy has reduced wetting and total heat flux.

Figure 11 further shows the results of tests 16-23 in which MO6 steel shells were deposited on smooth nickel-

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phosphorous alloy substrates which all had a 10% phosphorous content but in which one of the substrates had been subjected to annealing at 400°C for 1.5 hours after electroless deposition and the other substrate was not subjected to any annealing. It will be seen that the substrate not subjected to annealing produced the high K-values as previously experienced in tests 1-9 whereas the annealed substrate produced much lower K-values comparable with those achieved with the plain nickel substrate.

Figures 12 is a photomicrograph of the shell deposited on the nickel substrate in test number 11, Figure 13 is a photomicrograph of the shell deposited on the annealed substrate in dip test number 18 and Figure 14 is a photomicrograph of the shell deposited on the unannealed nickel phosphorous alloy substrate in the same dip test number 18. It will be seen that the microstructures exhibited in the shells deposited on the nickel substrate in test 11 and the annealed substrate in test 18 are similar. In both cases the shells are relatively thin and have coarse microstructure exhibiting initial solidification into ferrite. The shell of Figure 14 as deposited onto the unannealed alloy substrate is very much thicker and exhibits the finer microstructure associated with the extremely high solidification rates achievable in accordance with the present invention which result in initial solidification directly into austenite.

Figure 8 further provides the results of tests 24-27 in which shells were deposited on a nickel-phosphorous alloy substrate having a 10% phosphorous content but only partially annealed at 400°C for 45 minutes as compared with a control substrate of nickel as previously used in tests 1-15. It will be seen that the partially annealed

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substrate resulted in K-values generally between those of the unannealed and annealed substrates of tests 16-23, further demonstrating the effect of an amorphous coating and the graded reduction of K-value and heat flux according to the degree to which a crystalline structure is present in the coating.

Figure 11 also provides results obtained from tests 29-31 in which shells were deposited on a nickel-phosphorous alloy substrate of 10% phosphorous content from a peritectic steel composition having a carbon content of 0.13%. Normally a steel of such composition cannot be cast with good surface quality by direct thin strip casting techniques because the steel solidifies simultaneously into  $\delta$  and  $\gamma$  ferrite phases and produces gross distortions in the solidifying shell. In the present tests however, the peritectic steel composition produced a shell demonstrating the same microstructure as previously achieved with M06 steels on the nickel-phosphorous alloy substrates and with the same K-values, demonstrating a similar heat flux on solidification.

The solidification structure of the shell of peritectic steel produced in test number 30 is shown in Figure 15 and the solidification structure of a shell of the same steel deposited onto a textured chrome substrate is shown in Figure 16. It will be seen that the structure of Figure 15 is much the same as that exhibited in Figures 9 and 14 and exhibits prior austenite grain boundaries demonstrating that the liquid carbon steel has solidified directly into austenite. Moreover, there is no indication of any ferrite growth even after solidification has progressed to the stage where the cooling rate has decreased. This indicates that when austenitic

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solidification is initiated in accordance with the invention in a strip casting process there will be a complete transformation into austenite without any reversion to ferrite growth, although there will of course  
5 be a subsequent transformation at lower temperatures after the strip has left the casting surface or surfaces.

In the practice of the invention the material of the casting surfaces of the rolls must have a melting temperature higher than the temperature of the casting  
10 surfaces during metal solidification. The temperature of the casting surfaces will be dependent on the wetting angle of the molten metal on the casting surfaces. More specifically, the temperature that the casting surface coating experiences will be higher as the wetting angle  
15 decreases. The coating material may therefore be chosen so as to provide a balance between high heat flux and rapid solidification and maintenance of a coating temperature which is safely below the melting temperature of the coating.

20 The results illustrated in Figures 8 and 11 for the unannealed nickel-phosphorous substrates show a progressive loss of performance due to erosion of the coating. For high temperature steel casting, other two metal amorphous coatings may be used in accordance with the invention. For  
25 selection of suitable coating it is necessary to take into account the melting temperature of the coating, the interface temperature during casting and the annealing temperature of the coating. Table 1 sets out the relevant criteria for a number of possible alloy coatings which  
30 might be used in accordance with the invention in the casting of thin strip steel.

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Table 1

Coating	T interface (C)	T melt (C)	T crystal (C)	Method of deposition
Ni-P	750	870	200	Electroless
Ni-B	750	1065 (1018)	--	Electroless/thermal spray
Mo-P	730	1650	431	Electroless
Mo-B	730	2180	--	PVD / CVD
Cr-B	780	1630	--	PVD / thermal spray / CVD
Ti-P	1082	1495	882	--
Ti-B	1082	1540	884	PVD / CVD
Ta-B	882	2390	2050?	PVD / CVD
W-B	707	1970	--	PVD / CVD
Co-P	843	1023	--	--
Co-B	843	1110	--	--
Zr-B		1680	863	PVD / thermal spray / CVD
Fe-P	983	1048	735	--
Fe-B	983	1174	912	CVD
V-B	980	1735	--	CVD

In table 1, the interface temperature has been  
5 calculated on the assumption of perfect contact of a steel  
metal at 1650°C with a coating of 25°C.

Figures 17 to 21 illustrate a twin roll continuous  
strip caster which may be operated in accordance with the  
present invention. This caster comprises a main machine  
10 frame 11 which stands up from the factory floor 12. Frame  
11 supports a casting roll carriage 13 which is  
horizontally movable between an assembly station 14 and a  
casting station 15. Carriage 13 carries a pair of parallel



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casting rolls 16 to which molten metal is supplied during a casting operation from a ladle 17 via a tundish 18 and delivery nozzle 19 to create a casting pool 30. Casting rolls 16 are water cooled so that shells solidify on the moving roll surfaces 16A and are brought together at the nip between them to produce a solidified strip product 20 at the roll outlet. This product is fed to a standard coiler 21 and may subsequently be transferred to a second coiler 22. A receptacle 23 is mounted on the machine frame adjacent the casting station and molten metal can be diverted into this receptacle via an overflow spout 24 on the tundish or by withdrawal of an emergency plug 25 at one side of the tundish if there is a severe malformation of product or other severe malfunction during a casting operation.

Roll carriage 13 comprises a carriage frame 31 mounted by wheels 32 on rails 33 extending along part of the main machine frame 11 whereby roll carriage 13 as a whole is mounted for movement along the rails 33. Carriage frame 31 carries a pair of roll cradles 34 in which the rolls 16 are rotatably mounted. Roll cradles 34 are mounted on the carriage frame 31 by interengaging complementary slide members 35, 36 to allow the cradles to be moved on the carriage under the influence of hydraulic cylinder units 37, 38 to adjust the nip between the casting rolls 16 and to enable the rolls to be rapidly moved apart for a short time interval when it is required to form a transverse line of weakness across the strip as will be explained in more detail below. The carriage is movable as a whole along the rails 33 by actuation of a double acting hydraulic piston and cylinder unit 39, connected between a drive bracket 40 on the roll carriage and the main machine

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frame so as to be actuatable to move the roll carriage between the assembly station 14 and casting station 15 and vice versa.

Casting rolls 16 are contra rotated through drive shafts 41 from an electric motor and transmission mounted on carriage frame 31. Rolls 16 have copper peripheral walls formed with a series of longitudinally extending and circumferentially spaced water cooling passages supplied with cooling water through the roll ends from water supply ducts in the roll drive shafts 41 which are connected to water supply hoses 42 through rotary glands 43. The roll may typically be about 500 mm diameter and up to 2000 mm long in order to produce 2000 mm wide strip product.

Ladle 17 is of entirely conventional construction and is supported via a yoke 45 on an overhead crane whence it can be brought into position from a hot metal receiving station. The ladle is fitted with a stopper rod 46 actuatable by a servo cylinder to allow molten metal to flow from the ladle through an outlet nozzle 47 and refractory shroud 48 into tundish 18.

Tundish 18 is also of conventional construction. It is formed as a wide dish made of a refractory material such as magnesium oxide (MgO). One side of the tundish receives molten metal from the ladle and is provided with the aforesaid overflow 24 and emergency plug 25. The other side of the tundish is provided with a series of longitudinally spaced metal outlet openings 52. The lower part of the tundish carries mounting brackets 53 for mounting the tundish onto the roll carriage frame 31 and provided with apertures to receive indexing pegs 54 on the carriage frame so as to accurately locate the tundish.

Delivery nozzle 19 is formed as an elongate body

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made of a refractory material such as alumina graphite. Its lower part is tapered so as to converge inwardly and downwardly so that it can project into the nip between casting rolls 16. It is provided with a mounting bracket  
5 60 whereby to support it on the roll carriage frame and its upper part is formed with outwardly projecting side flanges  
55 which locate on the mounting bracket.

Nozzle 19 may have a series of horizontally spaced generally vertically extending flow passages to produce a  
10 suitably low velocity discharge of metal throughout the width of the rolls and to deliver the molten metal into the nip between the rolls without direct impingement on the roll surfaces at which initial solidification occurs. Alternatively, the nozzle may have a single continuous slot  
15 outlet to deliver a low velocity curtain of molten metal directly into the nip between the rolls and/or it may be immersed in the molten metal pool.

The pool is confined at the ends of the rolls by a pair of side closure plates 56 which are held against  
20 stepped ends 57 of the rolls when the roll carriage is at the casting station. Side closure plates 56 are made of a strong refractory material, for example boron nitride, and have scalloped side edges 81 to match the curvature of the stepped ends 57 of the rolls. The side plates can be  
25 mounted in plate holders 82 which are movable at the casting station by actuation of a pair of hydraulic cylinder units 83 to bring the side plates into engagement with the stepped ends of the casting rolls to form end closures for the molten pool of metal formed on the casting  
30 rolls during a casting operation.

During a casting operation the ladle stopper rod 46 is actuated to allow molten metal to pour from the ladle to

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the tundish through the metal delivery nozzle whence it flows to the casting rolls. The clean head end of the strip product 20 is guided by actuation of an apron table 96 to the jaws of the coiler 21. Apron table 96 hangs from  
5 pivot mountings 97 on the main frame and can be swung toward the coiler by actuation of an hydraulic cylinder unit 98 after the clean head end has been formed. Table 96 may operate against an upper strip guide flap 99 actuated by a piston and a cylinder unit 101 and the strip product  
10 20 may be confined between a pair of vertical side rollers 102. After the head end has been guided in to the jaws of the coiler, the coiler is rotated to coil the strip product 20 and the apron table is allowed to swing back to its inoperative position where it simply hangs from the machine  
15 frame clear of the product which is taken directly onto the coiler 21. The resulting strip product 20 may be subsequently transferred to coiler 22 to produce a final coil for transport away from the caster.

Full particulars of a twin roll caster of the kind  
20 illustrated in Figures 11 to 15 are more fully described in our United States Patents 5,184,668 and 5,277,243 and International Patent Application PCT/AU93/00593.

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CLAIMS

1. A method for continuously casting metal strip of the kind in which a casting pool of molten metal is formed in contact with a moving casting surface such that metal  
5 solidifies from the pool onto the moving casting surface, wherein the casting surface is provided by a solid coating on a heat conductive body and the coating is formed of a material such that the wetting angle of said molten metal on the casting surface is less than  $40^\circ$  and which has  
10 melting temperature greater than the temperature of the casting surface during metal solidification.
2. A method as claimed in claim 1, wherein the coating is formed of a material such that the wetting angle of the molten metal on the casting surface is less than  $20^\circ$ .
- 15 3. A method as claimed in claim 1 or claim 2, wherein the coating surface has an Arithmetic Mean Roughness Value ( $R_a$ ) of less than 10 microns.
4. A method as claimed in any one of the preceding claims, wherein the molten metal is molten steel.
- 20 5. A method as claimed in claim 4, wherein the steel solidifies into a single phase solid structure on the casting surface.
6. A method as claimed in any one of the preceding claims, wherein the coating material is at least partially  
25 amorphous.
7. A method as claims in claim 6, wherein the coating material is substantially totally amorphous.
8. A method as claimed in any one of the preceding claims, wherein the coating material is comprised of an  
30 alloy of two metals.
9. A method as claimed in claim 8, wherein one of said two metals is phosphorous.

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10. A method as claimed in claim 9, wherein the other of said two metals is nickel.
11. A method as claimed in any one of claims 8 to 10, wherein said alloy is a substantially eutectic alloy.
- 5 12. A method as claimed in any one of the preceding claims, wherein the molten metal has a substantially eutectic composition.
13. A method as claimed in any one of the preceding claims, wherein the heat conductive body is a copper or  
10 copper alloy body.
14. A method for continuously casting steel strip of the kind in which a casting pool of molten steel is formed in contact with a moving casting surface such that steel solidifies from the casting pool onto the moving casting  
15 surface, wherein the casting surface is provided by a solid coating on a heat conductive body and the coating is formed of a material such that the wetting angle of the molten metal on the casting surface is less than 40° and which has a melting temperature greater than the temperature of the  
20 casting surface during metal solidification, and wherein the steel solidifies into a single phase solid structure on the casting surface which phase does not transform before the strip has left the casting surface.
15. A method as claimed in claim 14, wherein said steel  
25 has a carbon equivalent content of not more than 0.53% by weight and said single phase structure comprises dendrites of solid austenite.
16. A method as claimed in claim 15, wherein the steel has a substantially peritectic composition.
- 30 17. A method as claimed in claim 16, wherein the steel has a carbon content of about 0.13% by weight.
18. A method as claimed in any one of claims 14 to 17,

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wherein the coating material is comprised of an amorphous alloy of two metals.

19. A method as claimed in claim 18, wherein one of the two metals is phosphorous.

5 20. A method as claimed in claim 19, wherein the coating is a nickel-phosphorous alloy containing about 10% phosphorous.

21. A method as claimed in any one of claims 14 to 20, wherein the heat conductive body is a copper or copper  
10 alloy body.

22. A method as claimed in any one of claims 14 to 21, wherein the moving casting surface is one of a pair of such surfaces being the surfaces of a pair of casting rolls forming a nip between them, the casting pool being  
15 supported on the casting rolls above the nip and the strip being delivered downwardly from the nip with said single phase solid structure.

23. A method for continuously casting metal strip of the kind in which a casting pool of molten metal is formed  
20 in contact with a moving casting surface such that metal solidifies from the casting pool onto the moving casting surface, wherein the metal is of peritectic composition, the casting surface is provided by a solid coating on a heat conductive body and the coating is formed of a  
25 material such that the wetting angle of the molten metal on the casting surface is less than 40° and which has a melting temperature greater than the temperature of the casting surface during metal solidification, and wherein the metal solidifies into a single phase solid structure on  
30 the casting surface which phase does not transform before the strip has left the casting surface.

24. Apparatus for continuously casting metal strip

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comprising a casting roll having a casting surface to contact a casting pool of molten metal and means to cool the casting surface of the casting roll to cause metal to solidify thereon, wherein the roll surface is formed by a solid coating on a heat conductive body of the roll which  
5 coating is comprised of a substantially amorphous alloy of two metals.

25. Apparatus as claimed in claim 24, wherein one of the two metals is phosphorous.

10 26. Apparatus as claimed in claim 25, wherein the coating alloy is a nickel-phosphorous alloy.

27. Apparatus as claimed in claim 26, wherein the coating alloy contains about 10% phosphorous.

28. A casting roll comprising a heat conductive  
15 cylindrical roll body covered by a solid coating defining a cylindrical metal casting surface, wherein the coating is comprised of a substantially amorphous alloy of two metals.

29. A casting roll as claimed in claim 28, wherein one of the two metals is phosphorous.

20 30. A casting roll as claimed in claim 29, wherein the casting alloy is a nickel-phosphorous alloy.

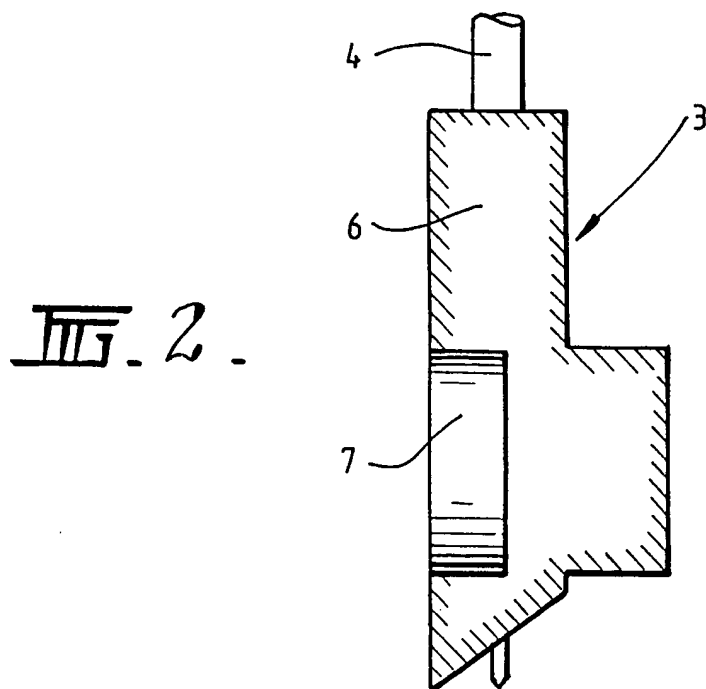
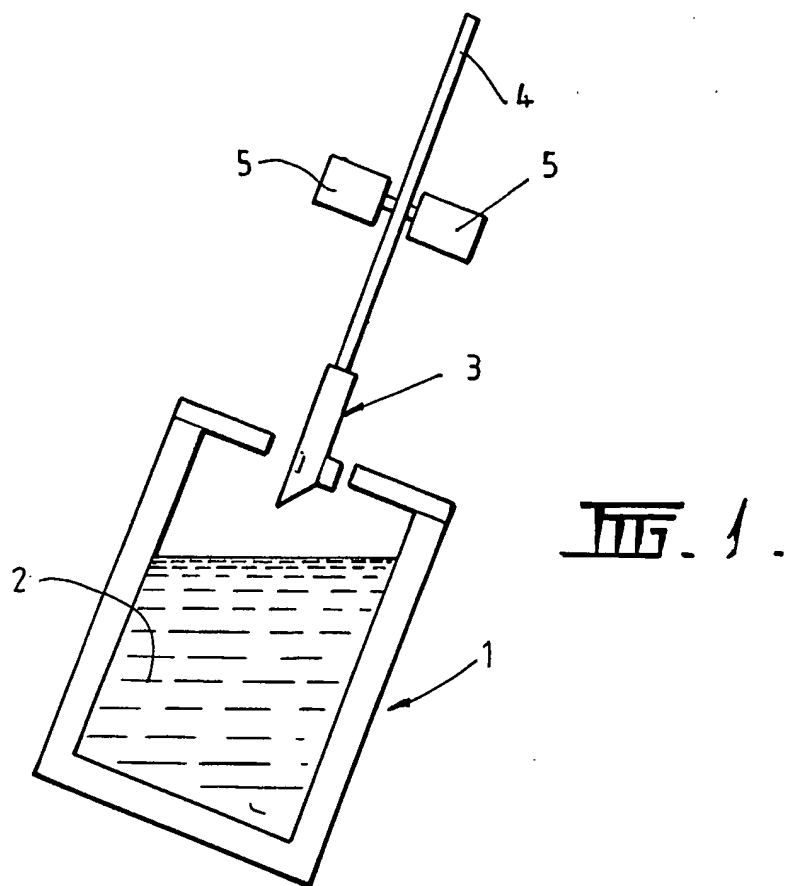
31. A casting roll as claimed in claim 30, wherein the coating alloy contains about 10% phosphorous.

32. A cast steel strip produced by continuous casting  
25 from a steel having a carbon equivalent content of not more than 0.53% by weight and having a microstructure resulting from direct solidification from molten metal into austenite prior to subsequent low temperature transformation.

33. A cast steel strip as claimed in claim 32, wherein  
30 the steel has a substantially peritectic composition.

34. A cast steel strip as claimed in claim 33, wherein the steel has a carbon content of about 0.13% by weight.





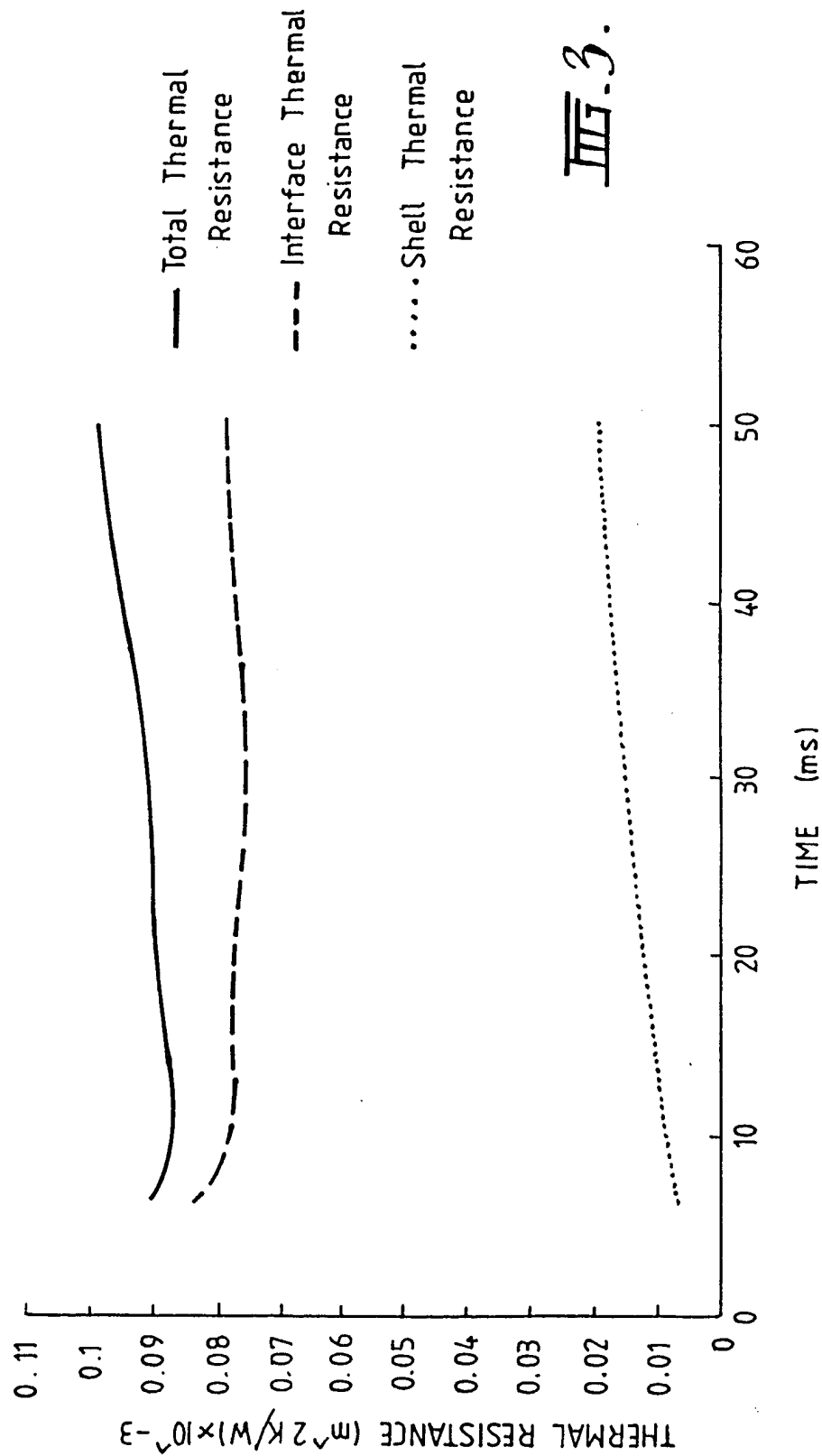
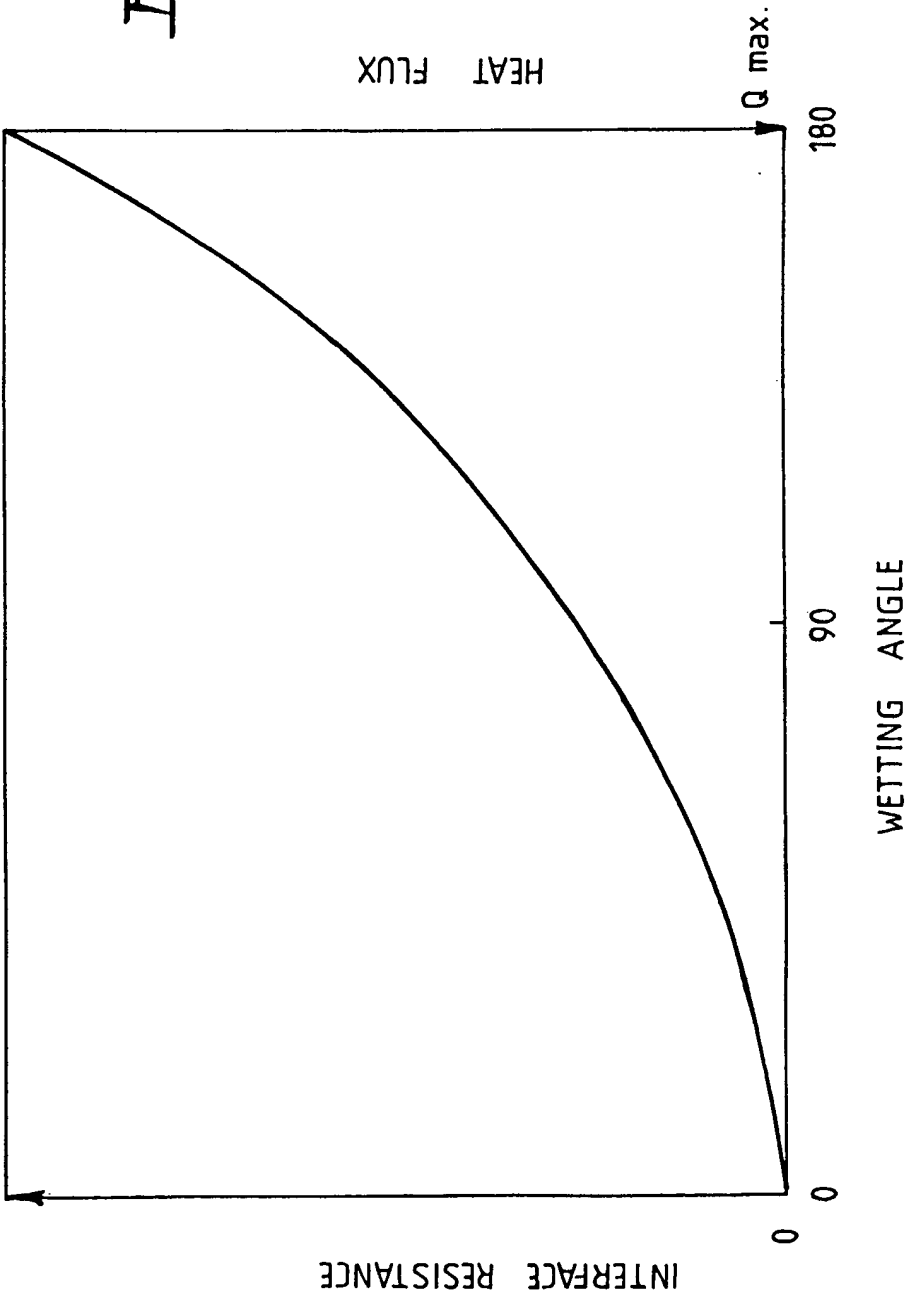


Fig. 3.

Fig. 4.



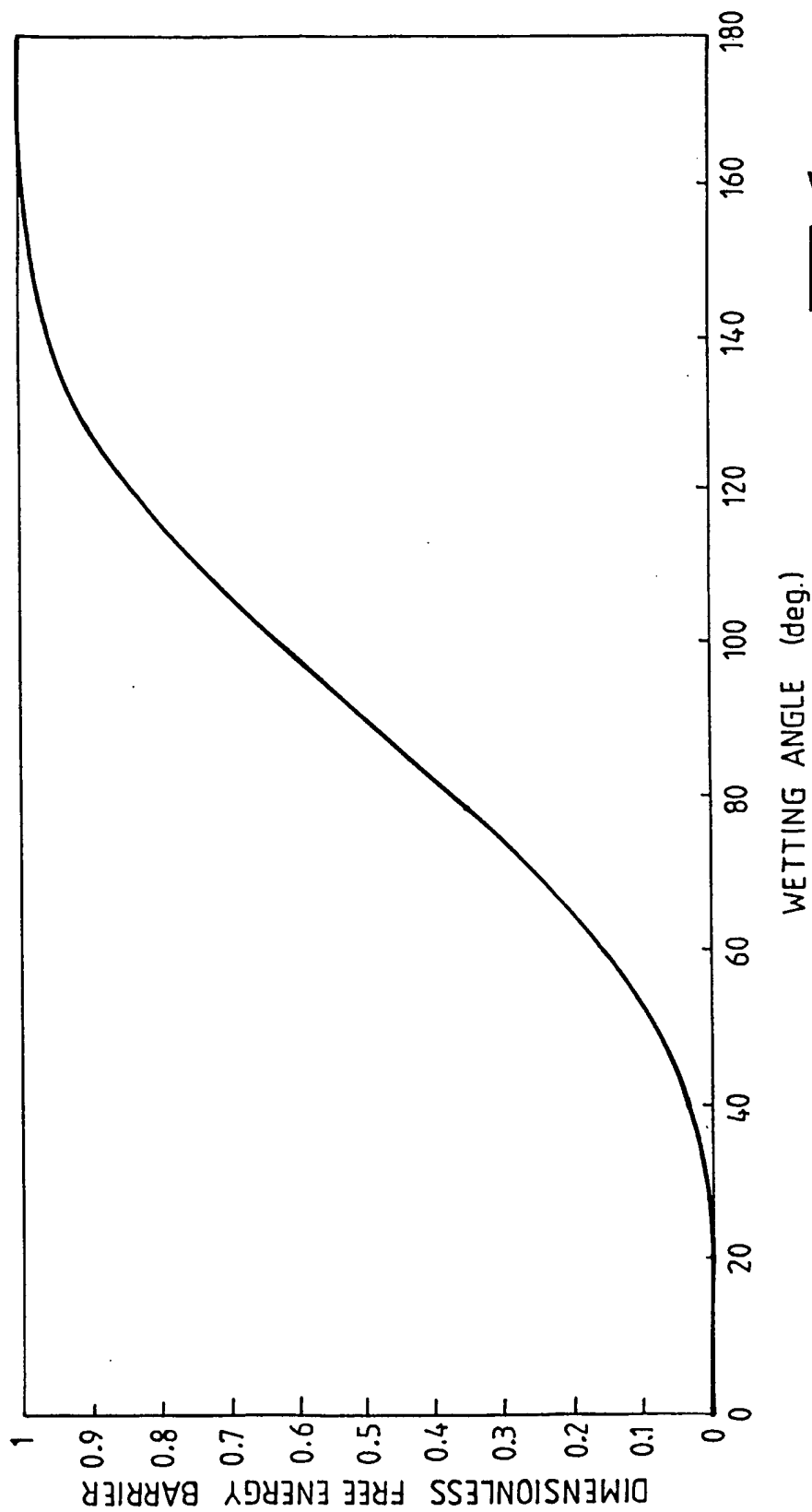


Fig. 5.

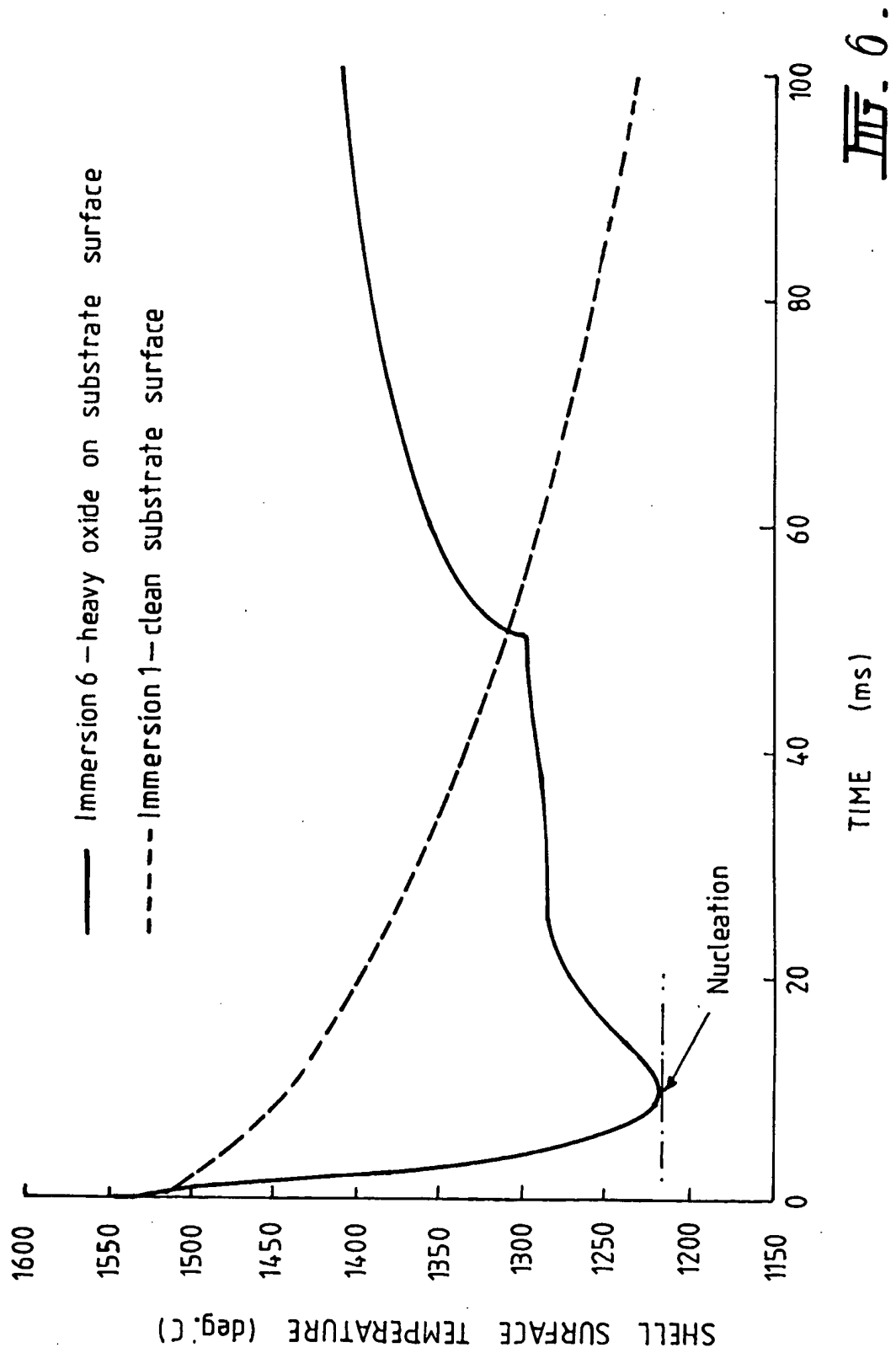
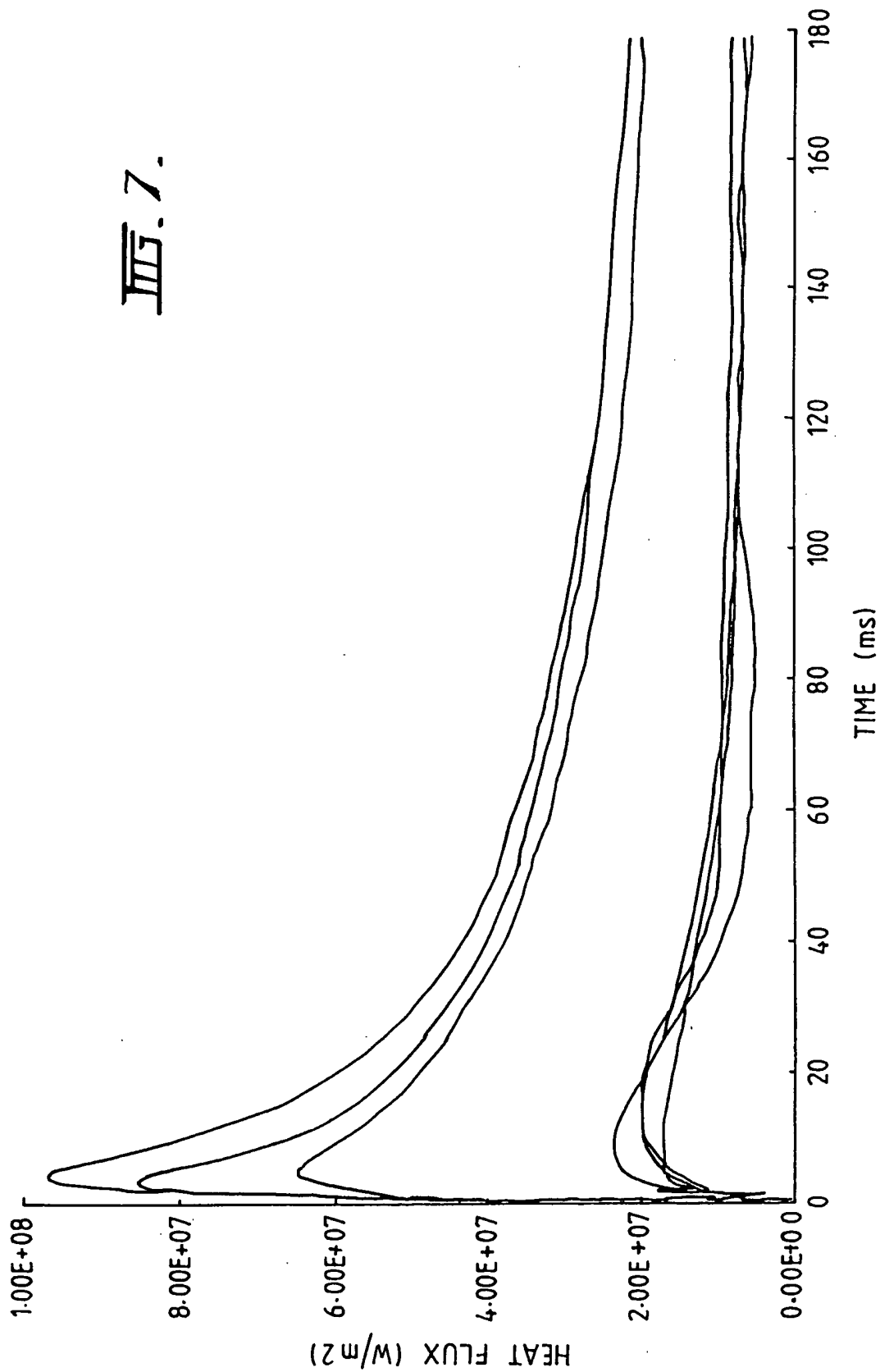
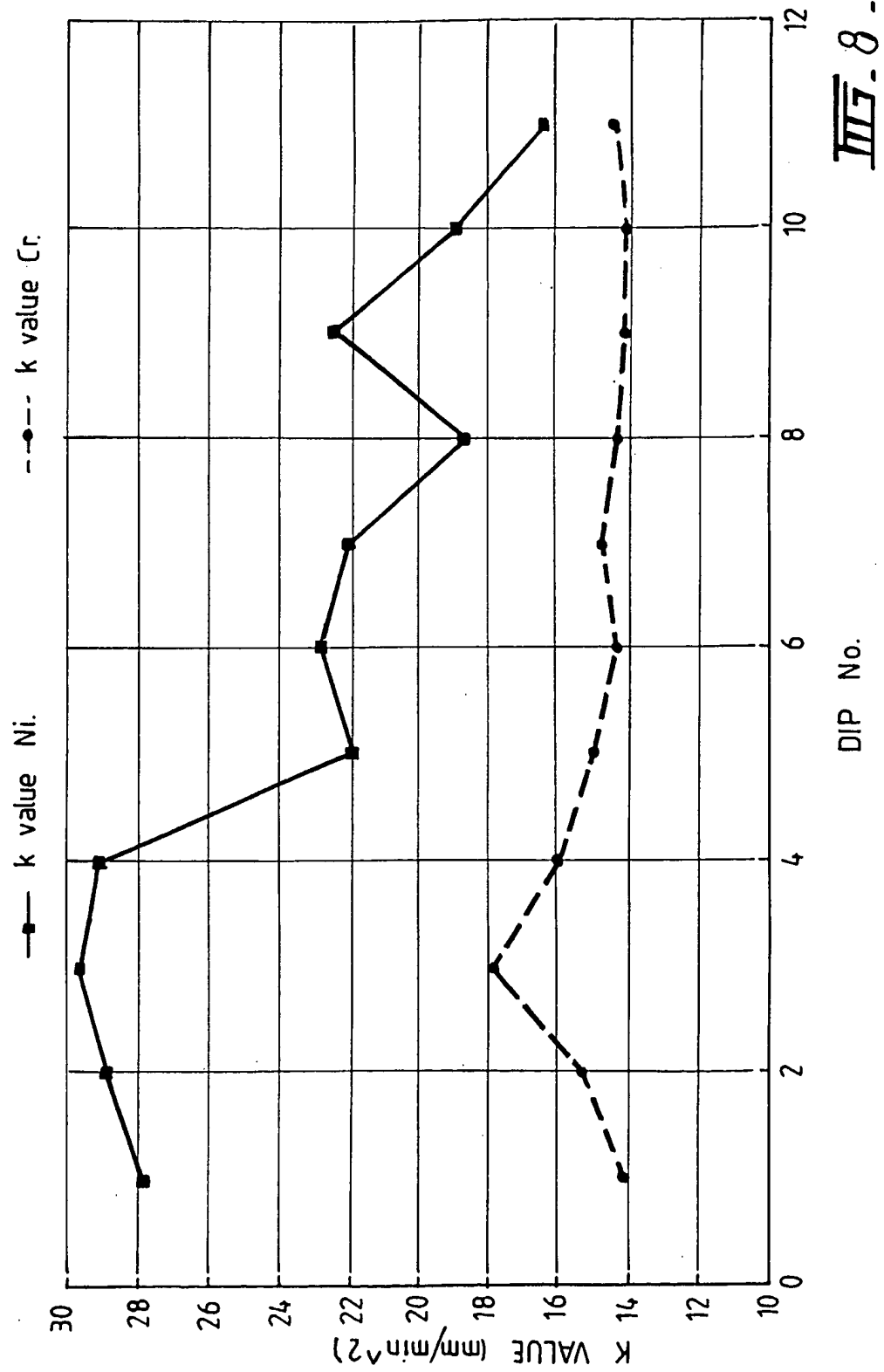


FIG. 6.

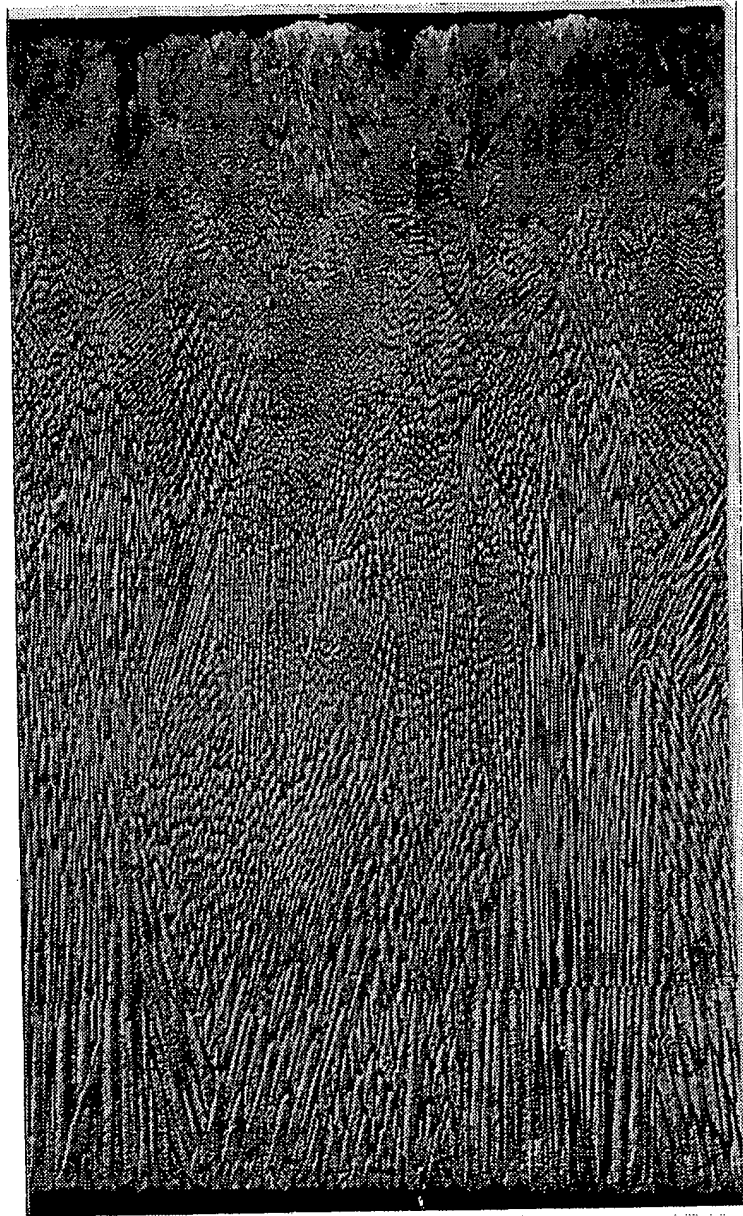
Fig. 7.





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Fig. 8.



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III 9.

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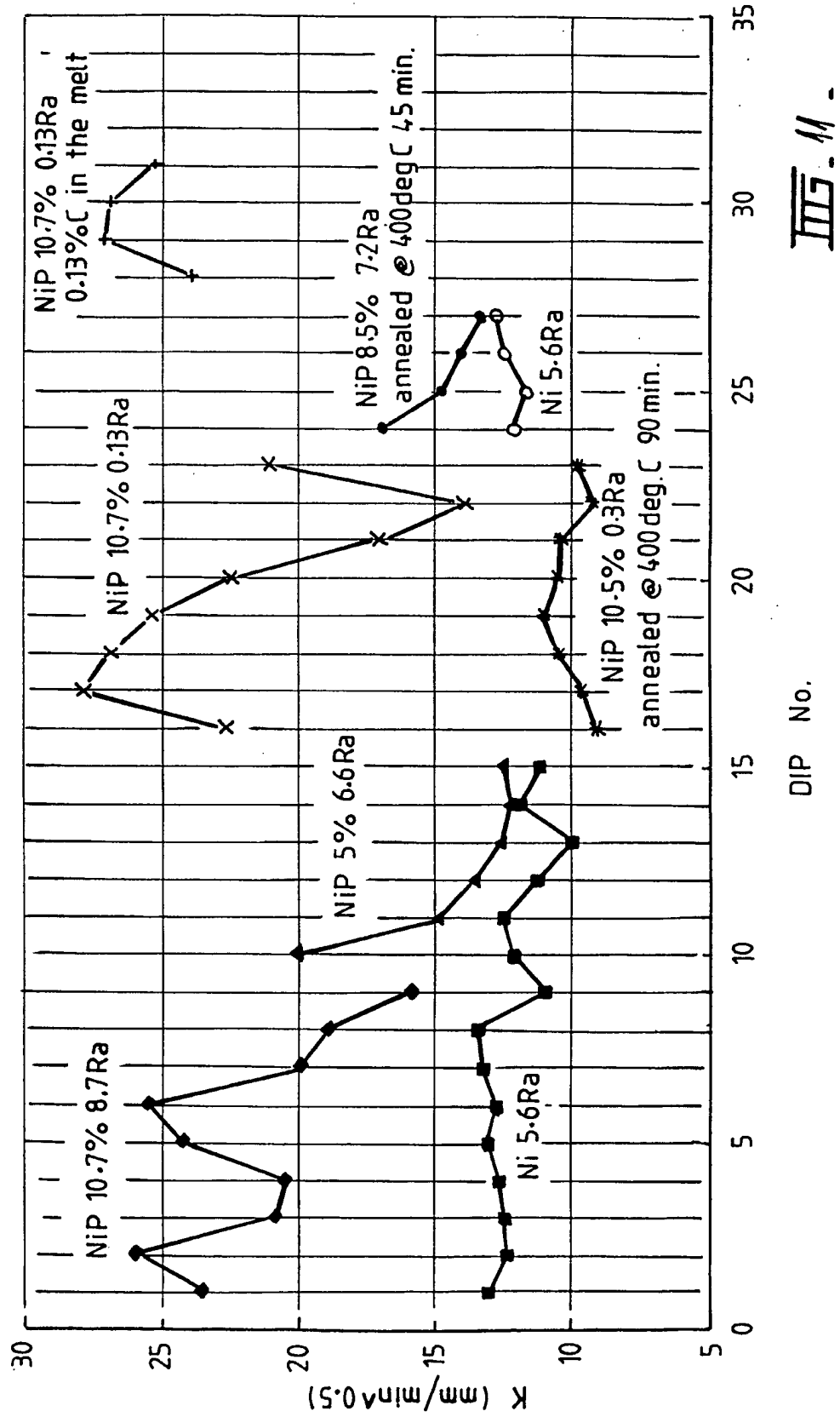


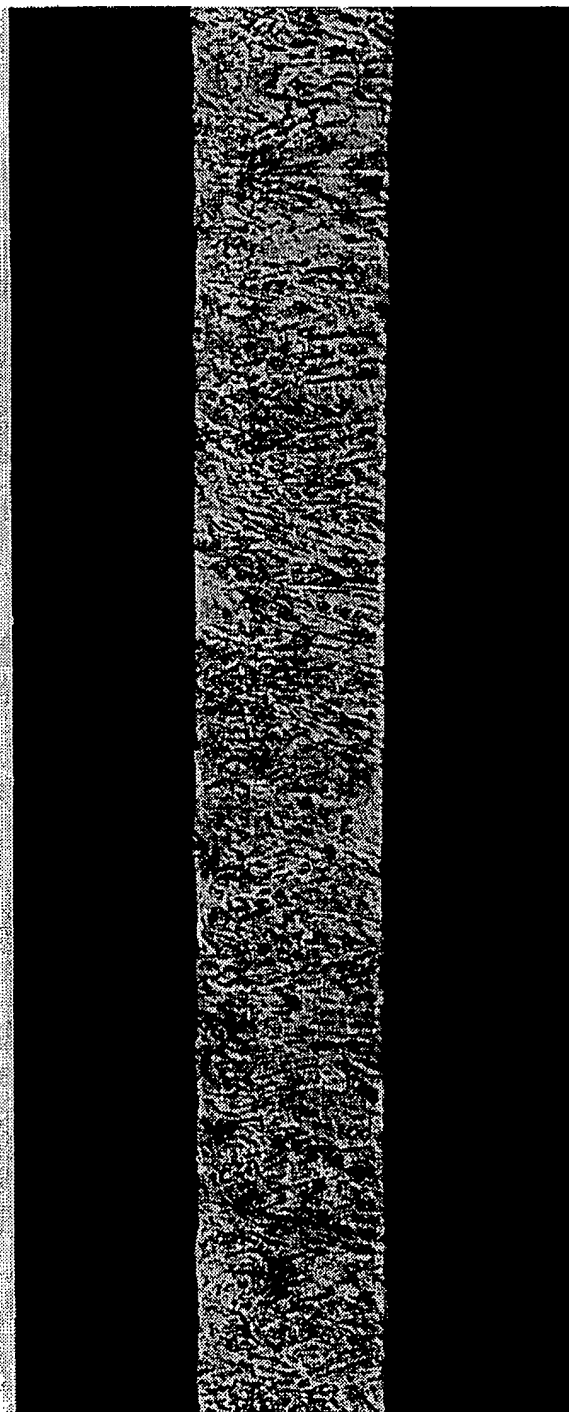


(x 100)

FIG. 10.

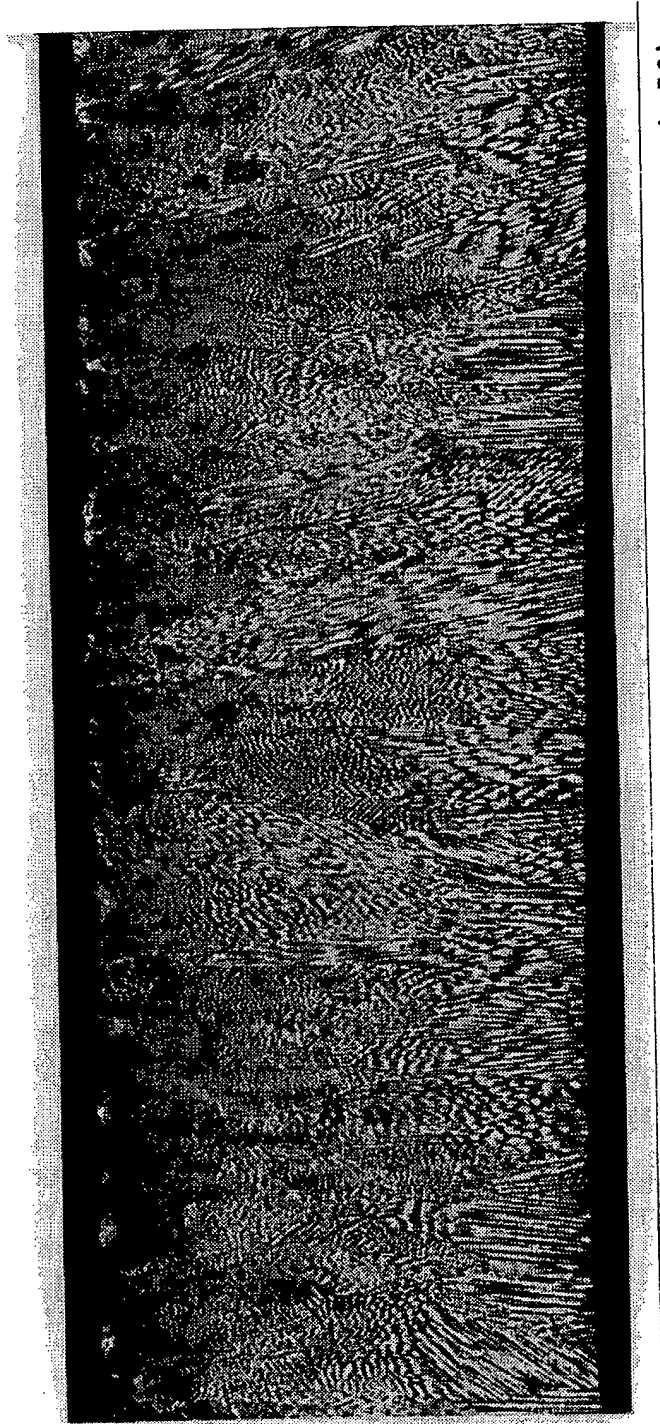
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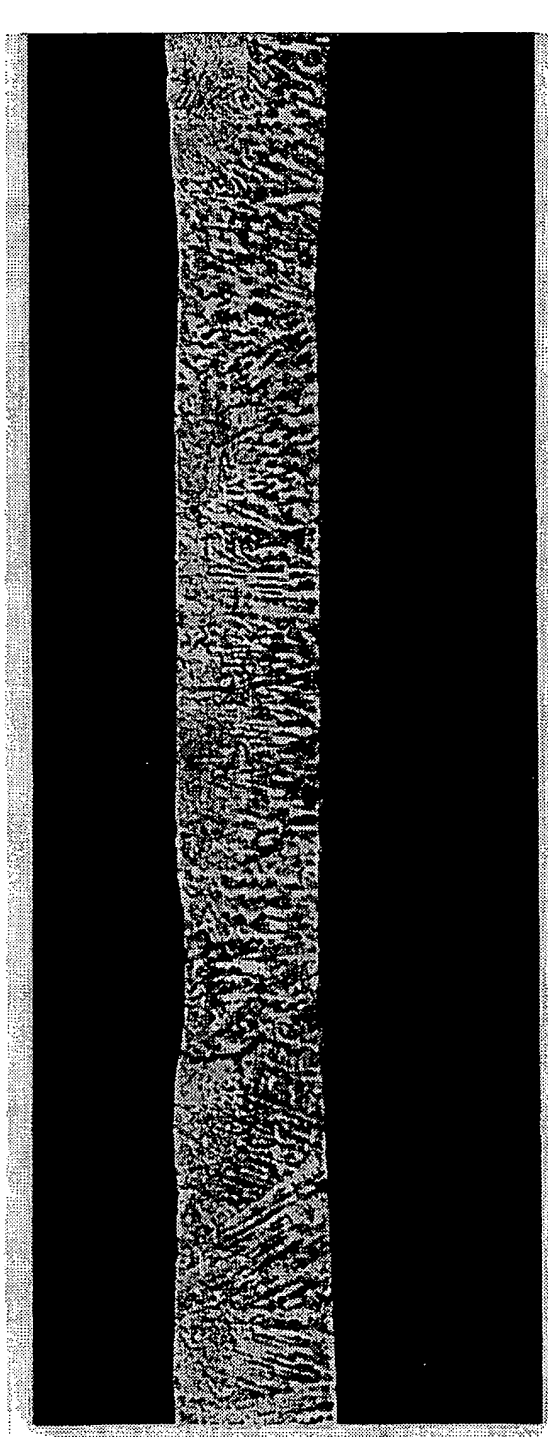
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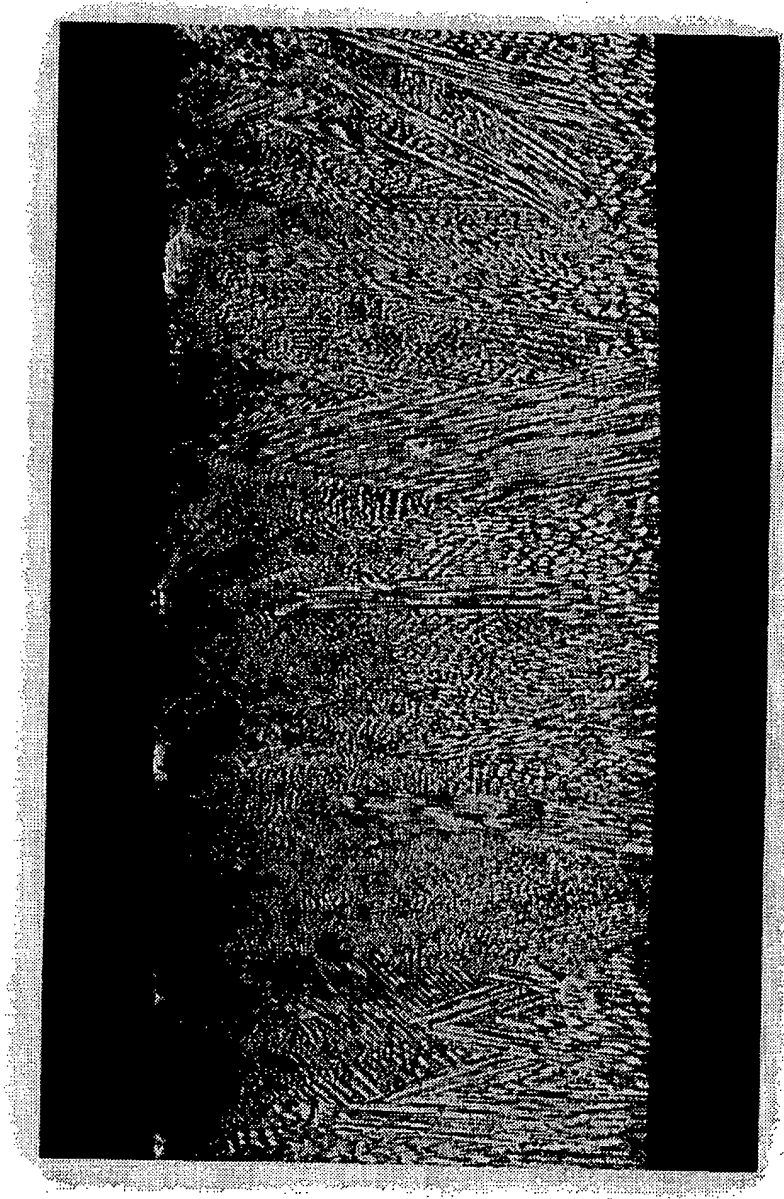
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III. 13.



(x 50)

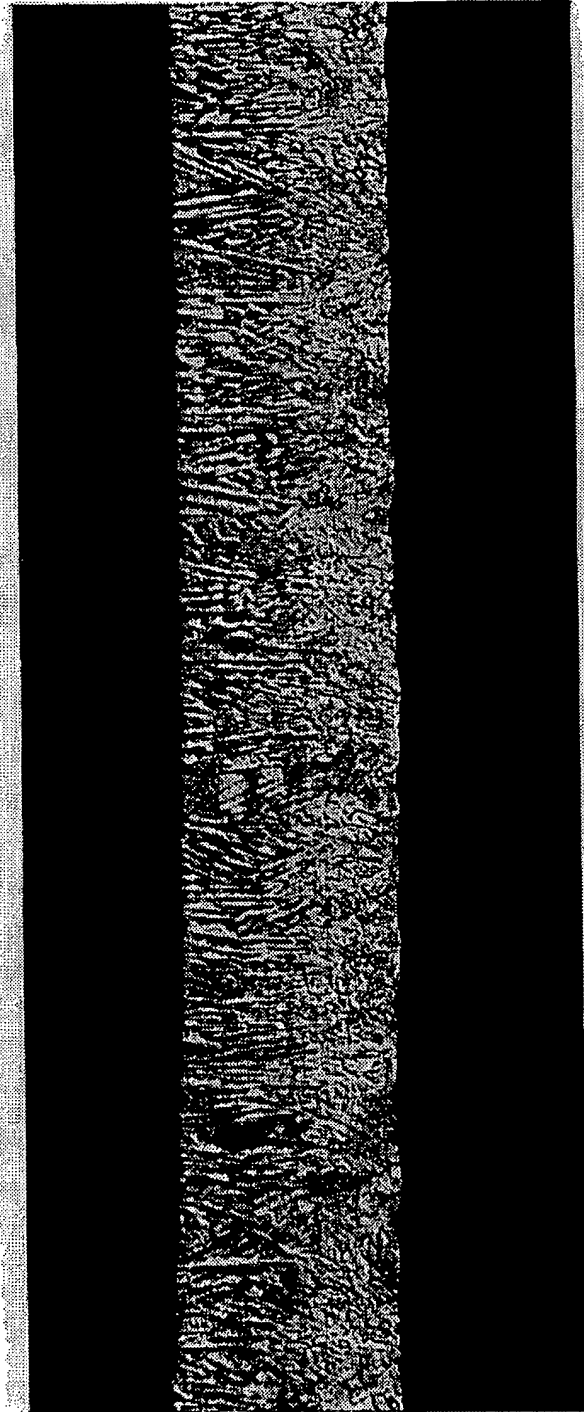
Fig. 14.



(x 50)

III-15 .

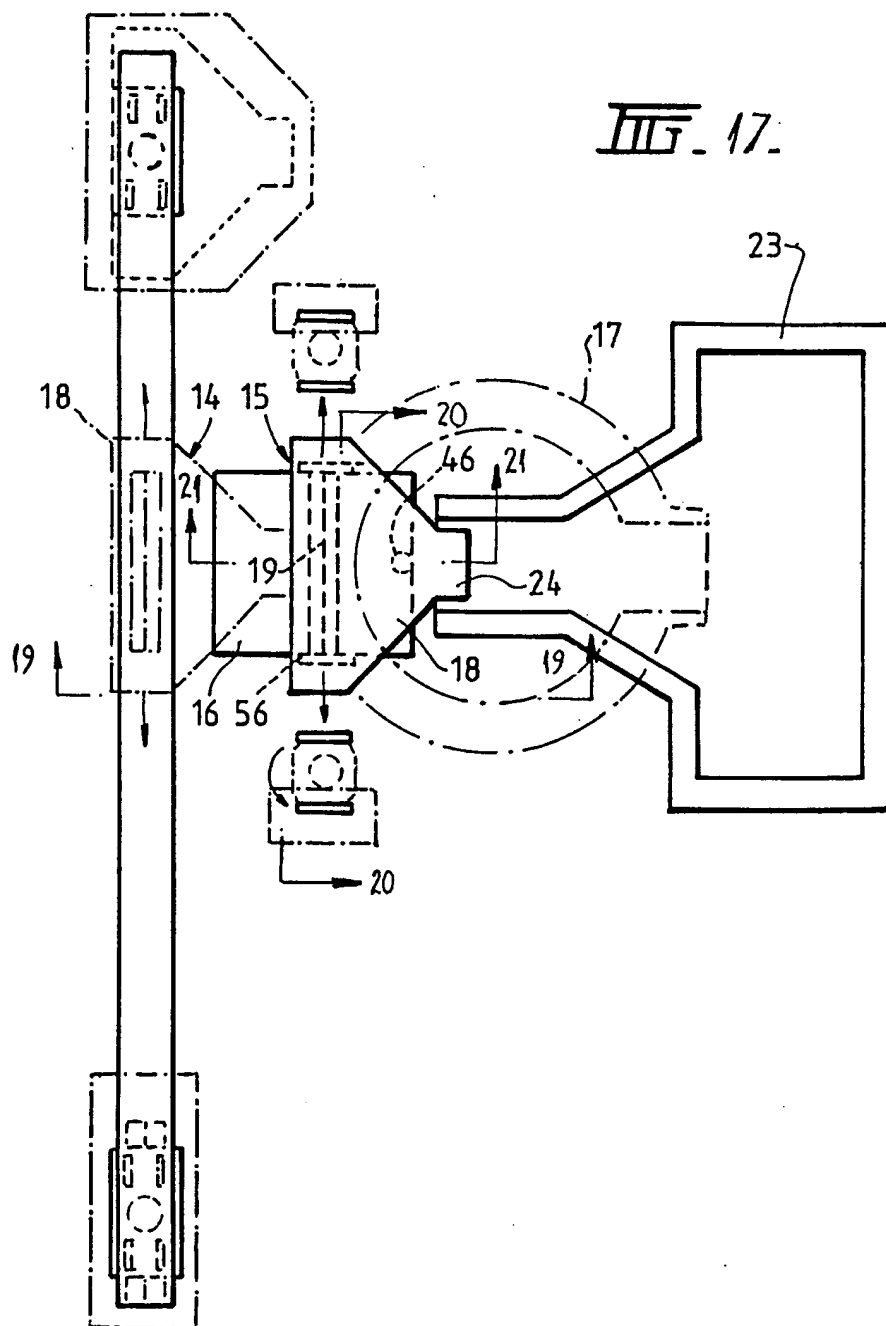
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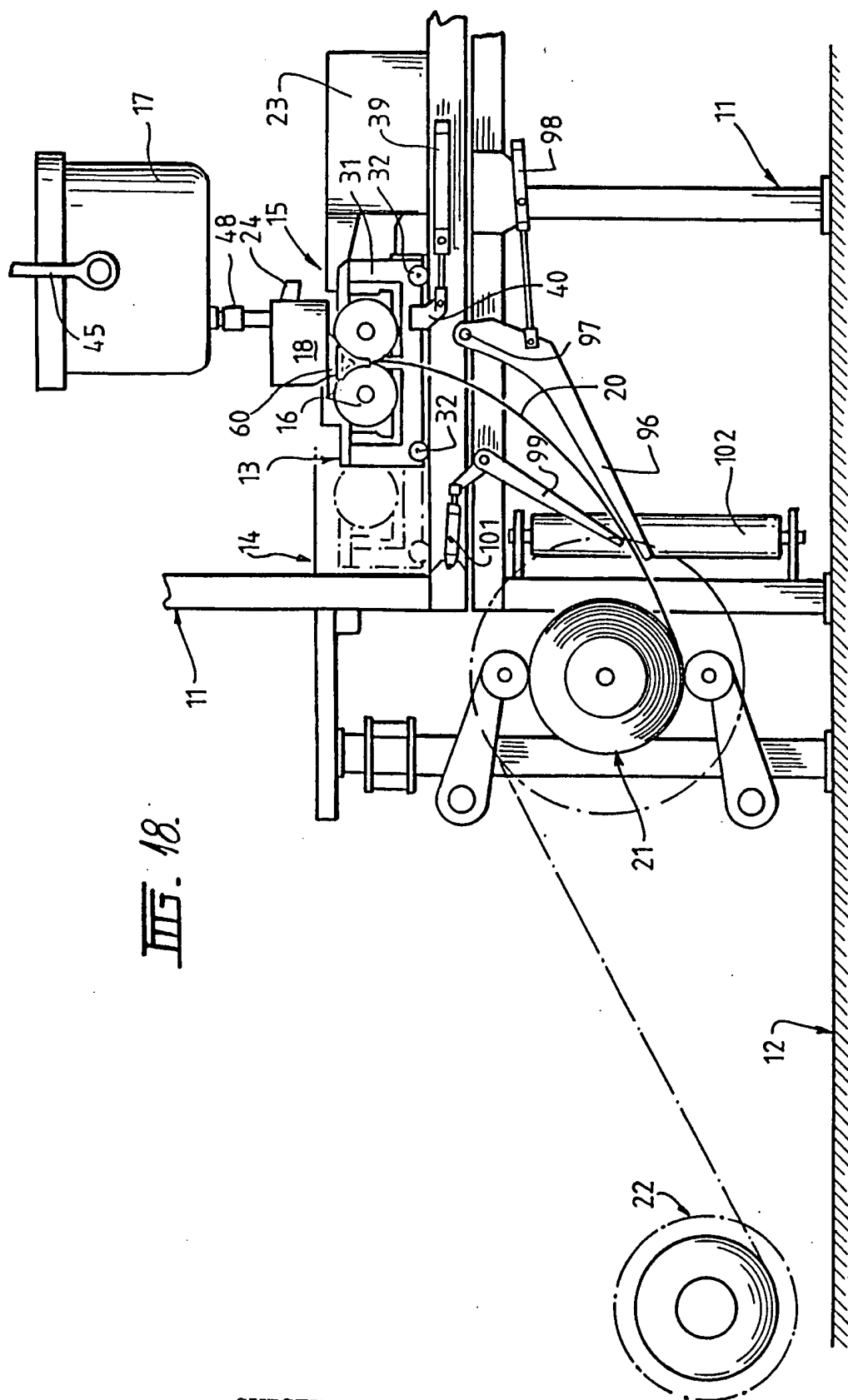
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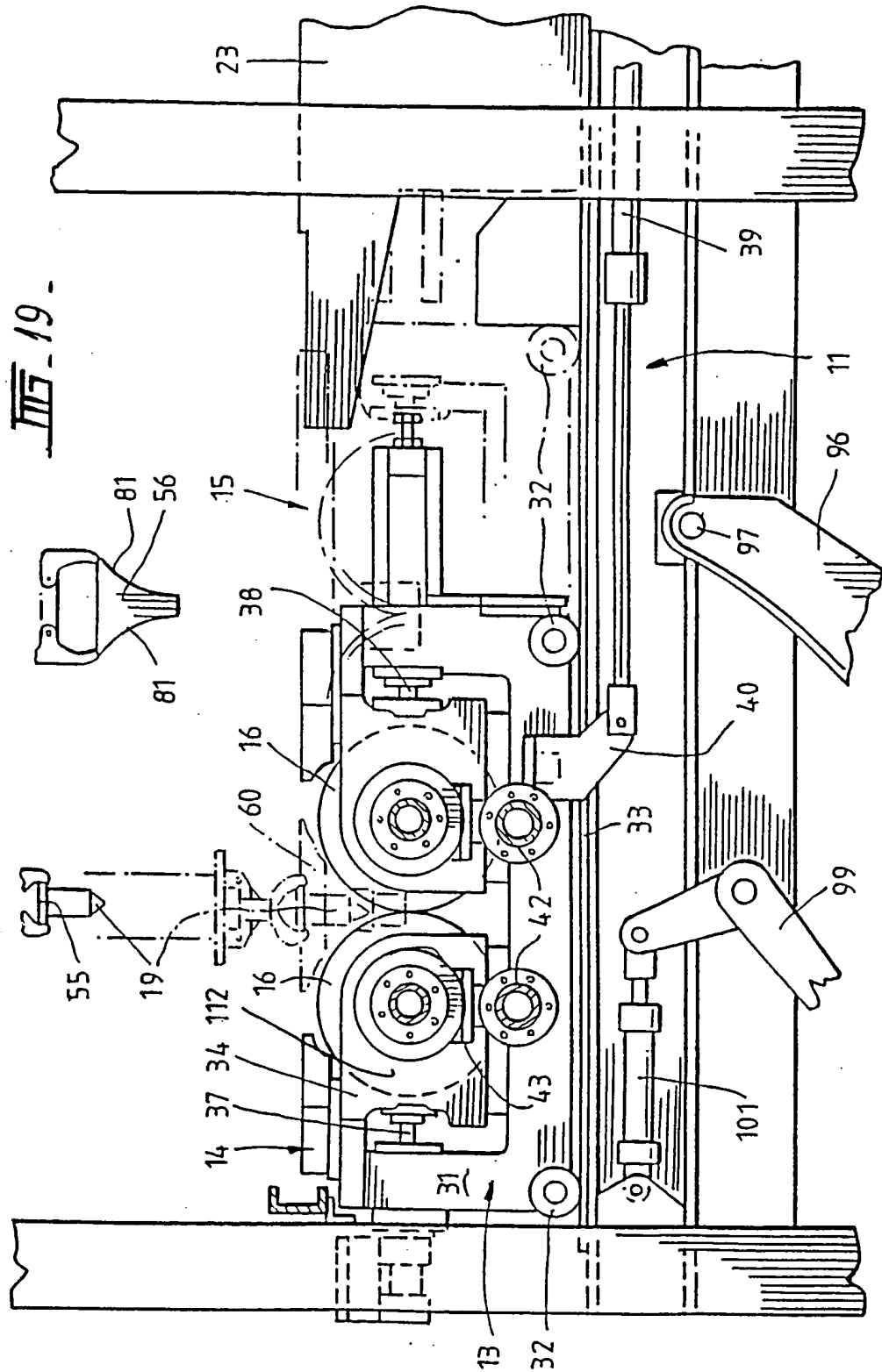
III - 16.

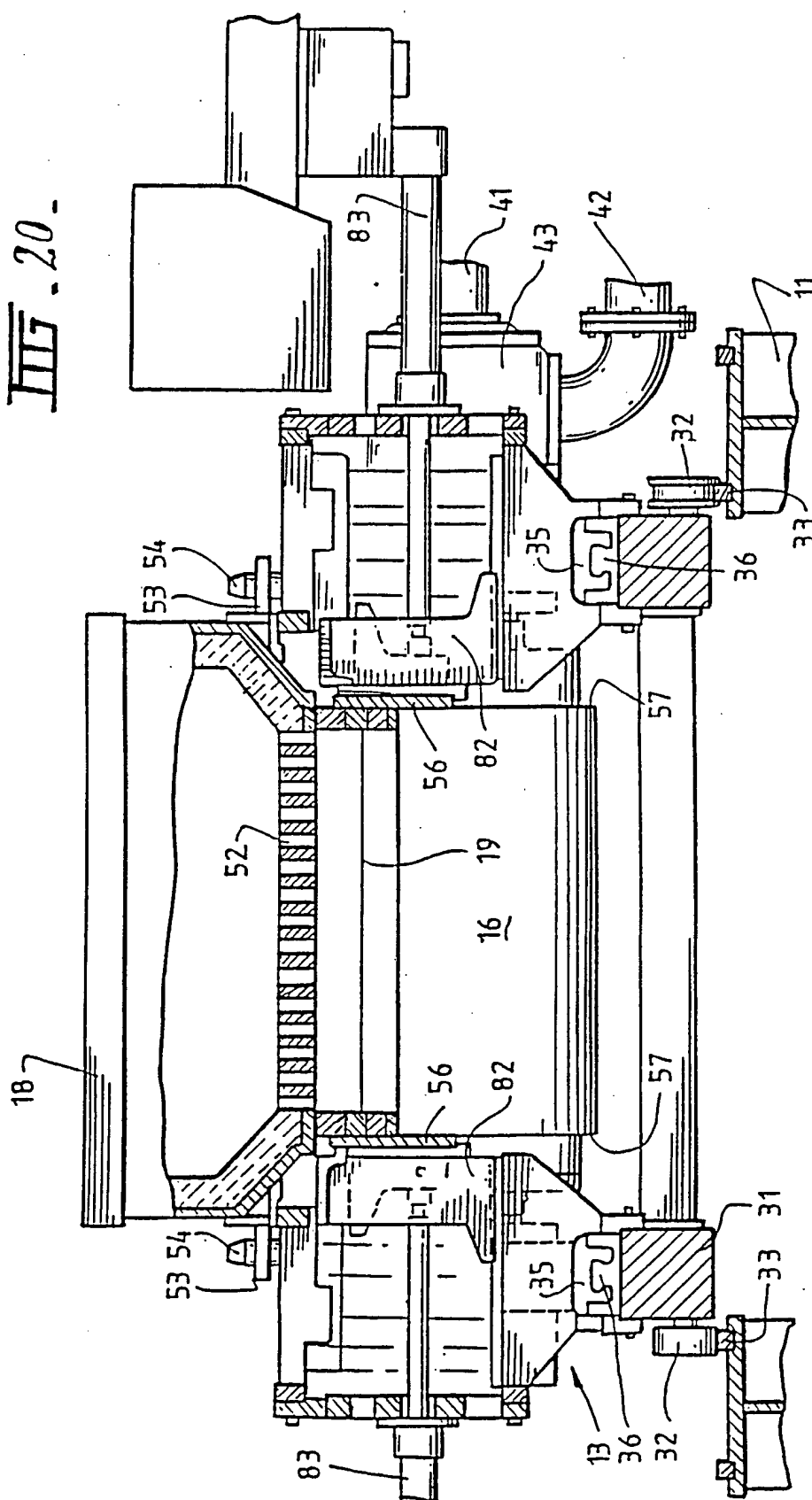
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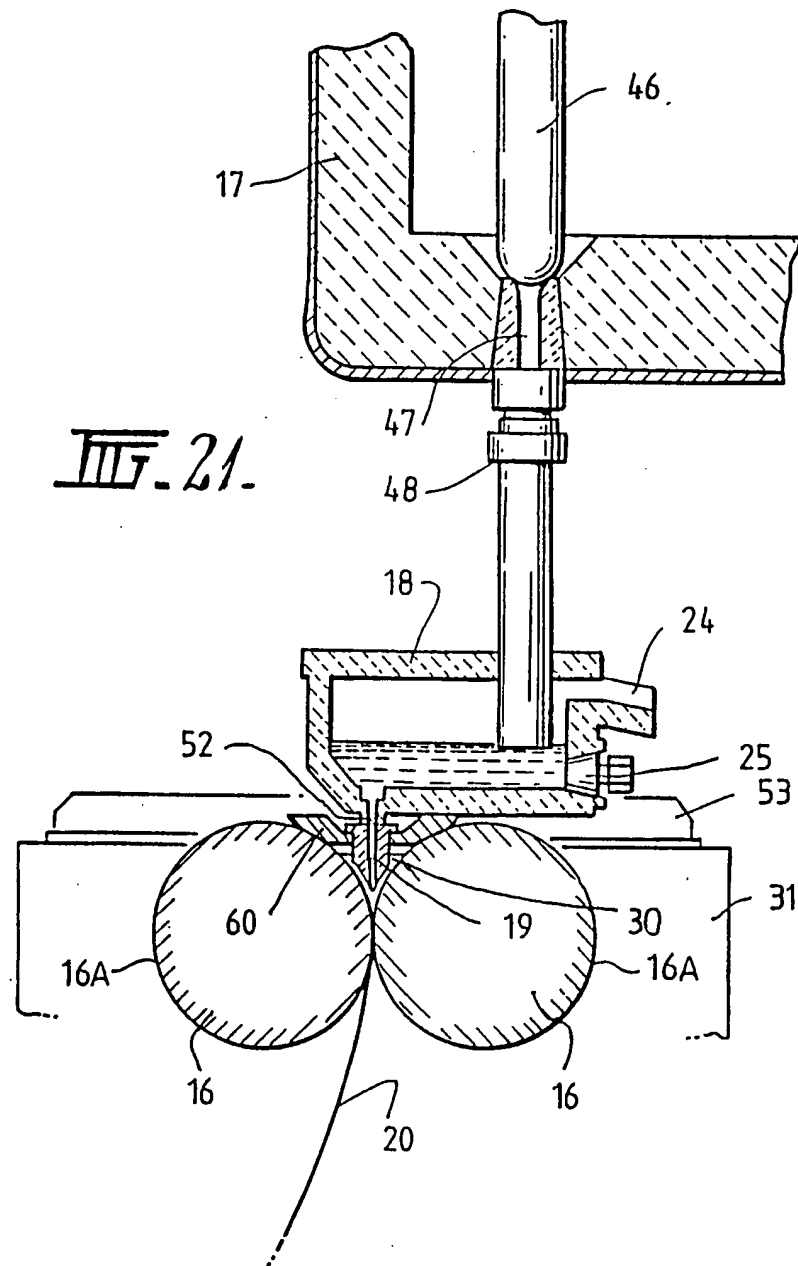









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# INTERNATIONAL SEARCH REPORT

International Application No.  
**PCT/AU 98/00412**

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int Cl <sup>6</sup> : <b>B22D 11/06, 11/14, 11/18.</b>		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) <b>IPC: B22D 11 MAIN GROUP.</b>		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched <b>AU: IPC as above.</b>		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  (see attached sheet)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<b>EP 732163 A2, (ISHIKAWAJIMA-HARIMA HEAVY INDUSTRIES CO. LTD. &amp; BHP STEEL (JLA) PTY. LTD.), 18 September 1996, (see Claims 1-4)</b>	<b>1-34</b>
A	<b>PATENT ABSTRACTS OF JAPAN, UNEXAMINED APPLICATIONS, {CD No. 9, B22, (1976-1993)}, JP 57/130750 A2, (NITTETSU HARD KABUSHIKI KAISHA), 13 August 1982.</b>	<b>1-34</b>
A	<b>PATENT ABSTRACTS OF JAPAN, UNEXAMINED APPLICATIONS, {CD No. 9, B22, (1976-1993)}, JP 02/160145 A2, (KAWASAKI STEEL CORPORATION &amp; KOUKA KUROOMU KABUSHIKI KAISHA), 20 June 1990.</b>	<b>1-34</b>
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 31 July 1998		Date of mailing of the international search report <b>11 AUG 1998</b>
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929		Authorized officer  <b>A. DAVIES</b> Telephone No.: (02) 6283 2072

**INTERNATIONAL SEARCH REPORT**

International Application No.

**PCT/AU 98/00412**

<b>C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<b>PATENT ABSTRACTS OF JAPAN, UNEXAMINED APPLICATIONS, {CD No. 1997-2[025]}, JP 08/281382 A2, (NIPPON STEEL CORPORATION), 29 October 1996.</b> -----	<b>1-34</b>
A	<b>PATENT ABSTRACTS OF JAPAN, UNEXAMINED APPLICATIONS, {CD No. 1997-3[026]}, JP 08/294751 A2, (NIPPON STEEL CORPORATION), 12 November 1996.</b> -----	<b>1-34</b>
A	<b>WO 94/12300 A1, {ISHIKAWAJIMA-HARIMA HEAVY INDUSTRIES CO. LTD. &amp; JOHN LYSAGHT (AUSTRALIA) LIMITED}, 9 June 1994, (see Claims 1-28)</b> -----	<b>1-34</b>
A	<b>WO 95/13889 A1, (BHP STEEL (JLA) PTY. LTD &amp; ISHIKAWAJIMA-HARIMA HEAVY INDUSTRIES CO. LTD.), 26 May 1995, (see Claims 1-13)</b> -----	<b>1-34</b>

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 98/00412

## Box

### Search on Electronic Data Base.

#### DERWENT WPAT.

SS1: B22D-11/IC (25651)

SS2: 1 AND (STRIP# OR BAND# OR SHEET# OR PLAT: (6270)

SS3: 2 AND (COAT: OR COVER: OR LAMINAT: OR SHEATH: OR OVERLA: OR LAYER: OR LAYER: OR SKIN: OR SUPERIMPOS: ENVELOP: OR SHROUD: ) (1200)

SS4: 3 AND (CONDUCT: OR TRANSFER: OR TRANSMI: OR TRANSPOS: OR DIFFUS: OR TRANSPLAC: OR TRANSLOC: OR MIGRAT: OR DISPERS: OR PASS:) (347)

#### JAPIO.

SS1: B22D-11/IC (18425)

SS2: 1 AND (STRIP# OR BAND# OR SHEET# OR PLAT: (5196)

SS3: 2 AND (COAT: OR COVER: OR LAMINAT: OR SHEATH: OR OVERLA: OR LAYER: OR LAYER: OR SKIN: OR SUPERIMPOS: ENVELOP: OR SHROUD: ) (1034)

SS4: 3 AND (CONDUCT: OR TRANSFER: OR TRANSMI: OR TRANSPOS: OR DIFFUS: OR TRANSPLAC: OR TRANSLOC: OR MIGRAT: OR DISPERS: OR PASS:) (297)

SS5 /C?

USER:

Sel steel

SS64 NOT 5 (257)

SS7: 6 AND ((WETTING (1) ANGLE)) (0)

SS8 /C?

USER:

6 AND (AMORPHOUS) (19)

SS9 /C

USER:

6 AND (PHASE) (15)

SS10 /C

USER:

8 OR 9 (23)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.  
PCT/AU 98/00412

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
EP	732163 A2	AU	45703/96 A1	BR	9601033 A	CA	2170312 AA
		CN	1136482 A	JP	08/252654 A2	NZ	286055 A
		US	5720336 A				
JP	57/130750 A2	NONE					
JP	02/160145 A2	NONE					
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